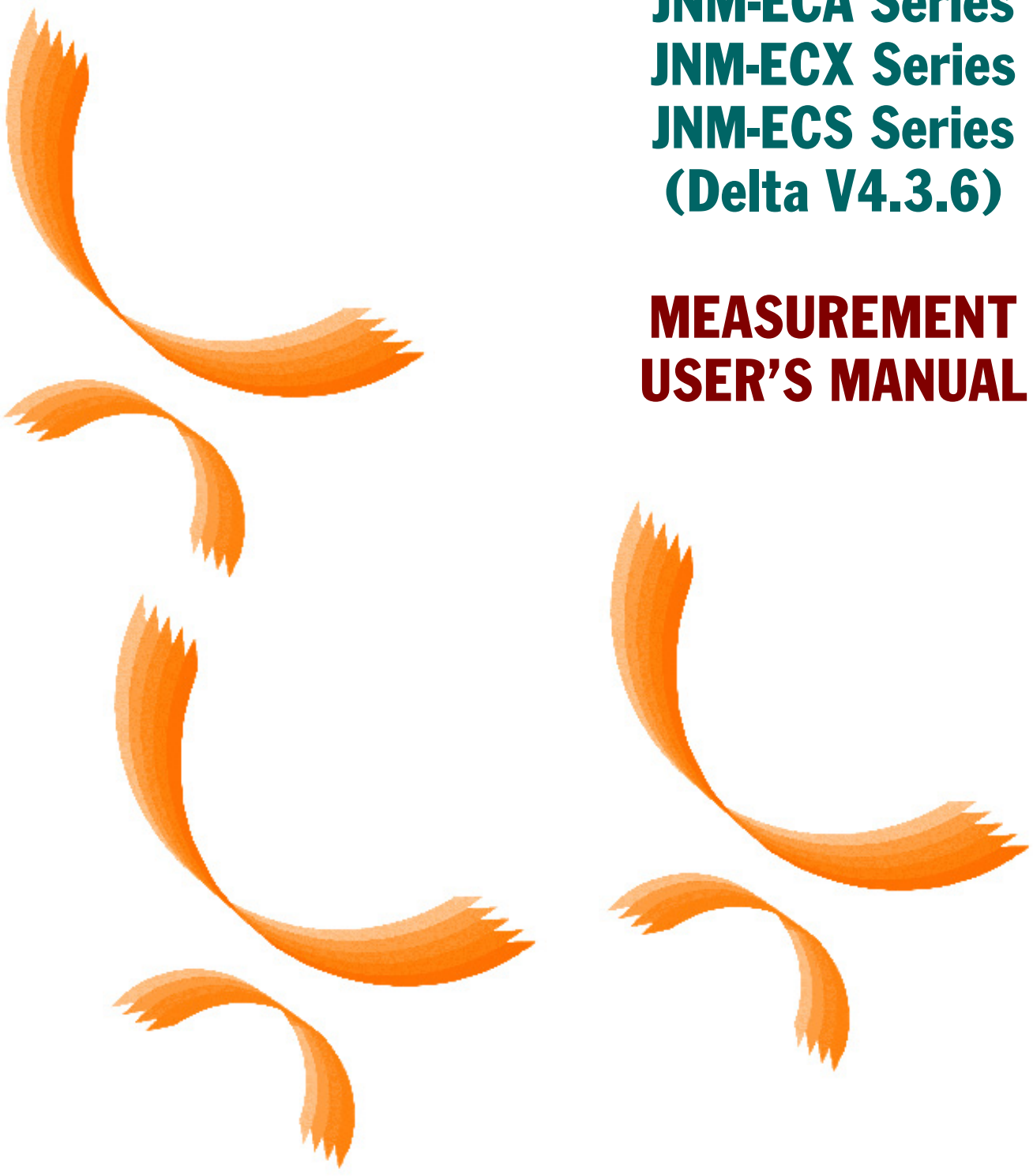
JNM-ECA Series
JNM-ECX Series
JNM-ECS Series
(Delta V4.3.6)

MEASUREMENT USER'S MANUAL



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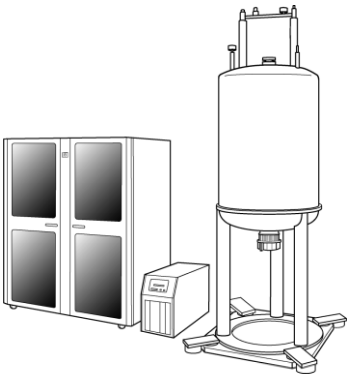

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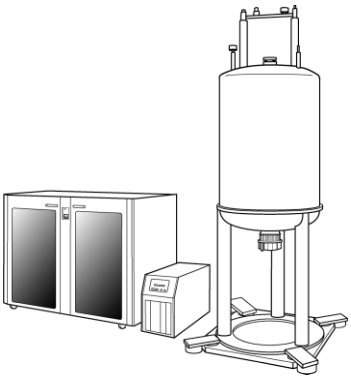
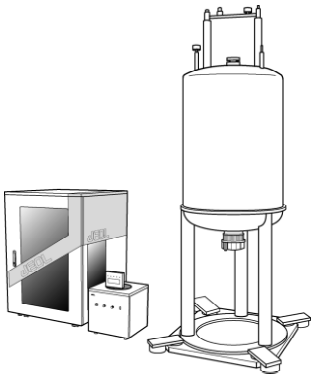


JNM-ECX Series



JNM-ECS Series

This manual explains how to adjust the system, how to set measurement conditions, and other procedures for performing various measurements using the ECA/ECX/ECS -NMR system.

Please be sure to read this instruction manual carefully, and fully understand its contents prior to the operation or maintenance for the proper use of the instrument.

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NOTATIONAL CONVENTIONS AND GLOSSARY

General notations

– CAUTION – : Points where great care and attention is required when operating the device to avoid damage to the device itself.

✍ : Additional points to be remembered regarding the operation.

☞ : A reference to another section, chapter or manual.

1, 2, 3 : Numbers indicate a series of operations that achieve a task.

◆ : A diamond indicates a single operation that achieve a task.

File: The names of menus, commands, or parameters displayed on the screen are denoted with **bold** letters.

File–Exit : A command to be executed from a pulldown menu is denoted by linking the menu name and the command name with a dash (–).
For example, **File–Exit** means to execute the **Exit** command by selecting it from the **File** menu.

Ctrl : Keys on the keyboard are denoted by enclosing their names in a box.

Mouse operation

Mouse pointer: An arrow-shaped mark displayed on the screen, which moves with the movement of the mouse. It is used to specify a menu item, command, parameter value, and other items. Its shape changes according to the situation.

Click: To press and release the left mouse button.

Double-click: To press and release the left mouse button twice quickly.

Drag: To hold down the left mouse button while moving the mouse.
To drag an item, you point to an item on the screen and then drag it using the mouse.

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1

FUNDAMENTALS OF DELTA

Chapter 1 describes the operation of the fundamental processing tool of the Delta program. The Delta program consists of various tools. Each tool uses two or more windows. Processing, analysis, and plot out for NMR data are performed using these tools.

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1.1 STARTING UP DELTA

This section assumes that operator is already logged into a workstation.

☞ Refer to the manual for the login procedure to a workstation.

■ When Delta icon is displayed on the desktop screen

◆ Double-click on the **Delta** icon.

The Delta program starts and the **Delta Console** appears.

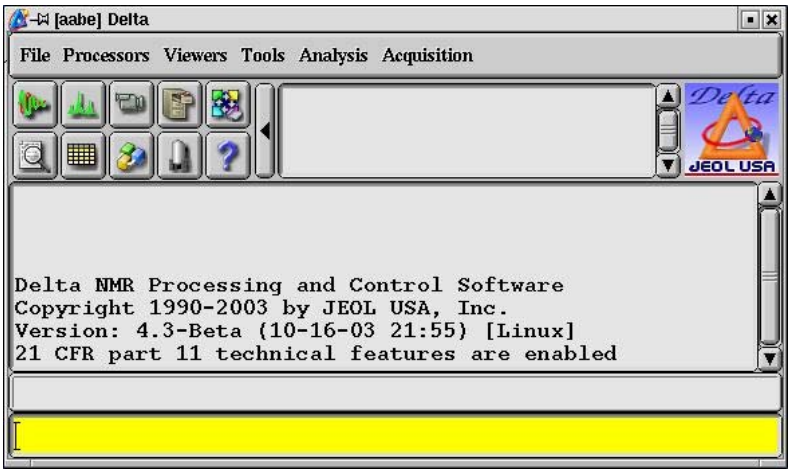
[aabe] Delta
File Processors Viewers Tools Analysis Acquisition
Delta
JEOL USA
Delta NMR Processing and Control Software
Copyright 1990-2003 by JEOL USA, Inc.
Version: 4.3-Beta (10-16-03 21:55) [Linux]
21 CFR part 11 technical features are enabled

Fig. 1.1 Delta Console window

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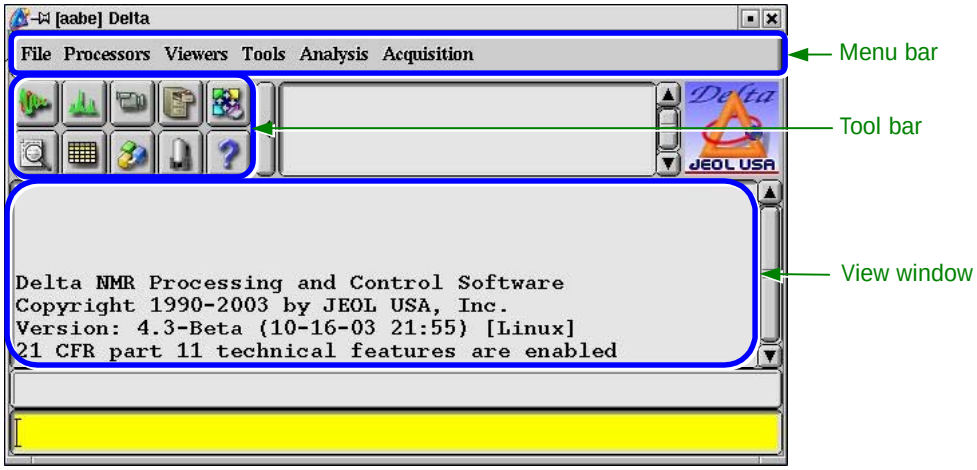
1.2 DELTA CONSOLE WINDOW

When you start the Delta program, the **Delta Console** window appears (☞Fig. 1.2). You can start all other tools from this window.
In the **Delta Console** window, you can start each Delta tool using the pull down menu for each item of the menu bar, or the tool bar button. Move the mouse pointer to the pull down menu or tool bar item, and click on the mouse left button.


[aabe] Delta
File Processors Viewers Tools Analysis Acquisition
Menu bar
Tool bar
JEOL USA
Delta NMR Processing and Control Software
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Version: 4.3-Beta (10-16-03 21:55) [Linux]
21 CFR part 11 technical features are enabled
View window

Fig. 1.2 Delta Console window

1.2.1 The menu bar in the Delta Console window

The list of items is displayed beneath of the title bar of the **Delta Console** window. This is called the “menu bar”. Select any function in this menu bar using the mouse.

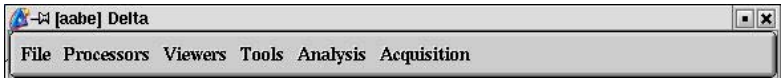

Fig. 1.3 Menu bar of the Delta Console window

■ Pull down menu

Each item of the menu bar has a “pull down menu”. When you select a menu bar item using the mouse left button the pull down menu appears (☞Fig. 1.5).
To select an item from the pull down menu, drag the mouse (with the left button of the mouse depressed), and releasing the left button of the mouse over the item you want to select.
If you select a pull down menu by mistake, after moving the mouse pointer away from the pull down menu, release the left mouse button.
The tool bar functions frequently used also appear as icons under the menu bar.

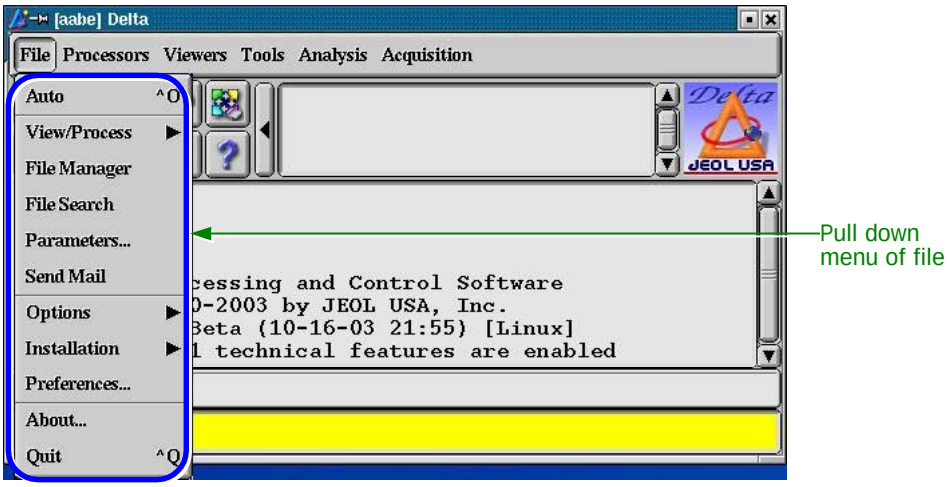

Fig. 1.4 Pull down menu

■ Accelerator key

An accelerator key is displayed to the right on the pull down menu. If you enter this key from the keyboard, you can quickly open a window or select an option.
In displayed an accelerator key, the "^" sign indicates the Ctrl key. For example, in the case of [^O], this means pressing the O key while pushing the Ctrl key.

Fig. 1.5 Accelerator key

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1.2.2 Tool Bar in the Delta Console Window

The icons located under the menu bar form the “tool bar”.
A picture of each function is displayed on each button. To select a button, move the mouse pointer onto a button and click the mouse left button.
Almost all buttons have the same function as the corresponding menu bar items.

Fig. 1.6 Tool bar in the Delta Console window

The following table explains the tool bar icon of the **Delta Console** window.

Icon	Button name	Explain
	Data processor	This tool is for NMR data processing. If you specify a file name, a **1D Processor** or **nD Processor** window opens according to the number of dimensions of data in the specified file. ☞ Refer to the separate PROCESSING USER’S MANUAL for details on the **1D Processor** and **nD Processor** window.
	Data slate	A data slate is a multipurpose NMR data display viewer. 1D, 2D, and 3D data can be displayed in a single window. Moreover, it can produce a print of two or more spectra on the one chart. ☞ For details, refer to the separate “PROCESSING USER’S MANUAL".
	Data viewer	The data viewer is the tool provided for the display of multi-dimensional NMR data. The contents of the window displayed change with the numbers of dimensions of the data. This is used for obtaining both the projection and the cross section of multi-dimensional NMR data.
	File manager	This is a tool for saving and managing the directory that is used in the Delta program and a file that is stored in the directory. If this tool is used, not only can it easily reference a file in the directory, but it can perform the copy, edit, deletion, change of name, and data conversion of a file.
	Presentation manager	A presentation manager is a tool for customizing the plot format of NMR data.
	Parameter viewer	A parameter viewer is a tool that displays information, such as a data set parameter, report, sequence, processing history, and an electronic signature.
	Spreadsheet	A spreadsheet is a tool that displays information about a peak, integration, and assignment in table format.
	Connection tool	A connection tool is to connect the display range of different data set. Connection is performed using the reference of an axis. You can associate any data sets regardless of the number of data points, observation width, and magnetic field strength. If connection is performed and the display range is changed to one data file, other related data will be automatically set to the same display range.
	Spectrometer control tool	A spectrometer control tool is a tool which connects and disconnects the host computer and the spectrometer.
	Help	The help button displays an electronic manual using Acrobat Reader®.

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2.1 SPECTROMETER CONTROL WINDOW

The **Spectrometer Control** window controls spectrometer connection and NMR measurement.

2.1.1 Starting the Spectrometer Control Window

Starts the **Spectrometer Control** window from the **Delta Console** window.

◆ Click on the button in the **Delta Console** window.
The **Spectrometer Control** window opens.

✍ If you select **Acquisition–Connect** in the menu bar, the **Spectrometer Control** window can also be started.

✍ In the **Delta Console** window, if you press the C key while pushing the Ctrl key, the **Spectrometer Control** window can start.

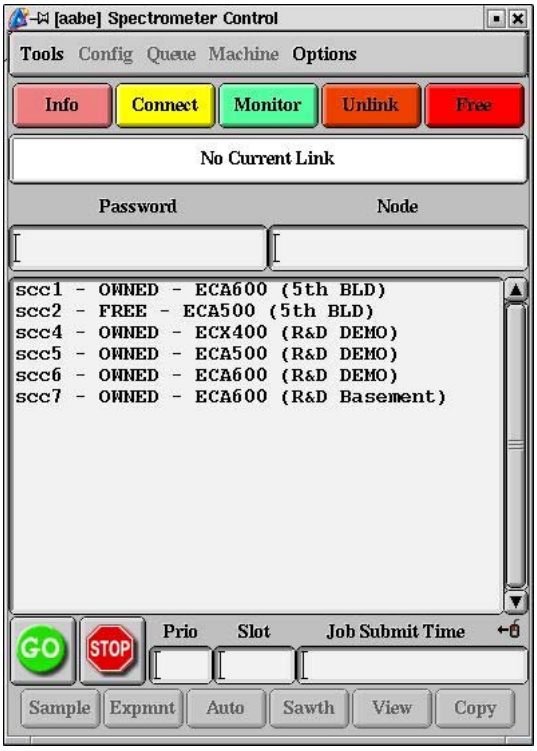

[aabe] Spectrometer Control
Tools Config Queue Machine Options
Info Connect Monitor Unlink Free
No Current Link
Password Node
scc1 - OWNED - ECA600 (5th BLD)
scc2 - FREE - ECA500 (5th BLD)
scc4 - OWNED - ECX400 (R&D DEMO)
scc5 - OWNED - ECA500 (R&D DEMO)
scc6 - OWNED - ECA600 (R&D DEMO)
scc7 - OWNED - ECA600 (R&D Basement)
GO
STOP
Prio Slot Job Submit Time
Sample Expmnt Auto Sawth View Copy

Fig. 2.1 Spectrometer Control window.

The **Spectrometer Control** window can control spectrometer function.

C I

2.1.2 Connecting and Releasing Spectrometer

The connectable spectrometers are listed in the **Spectrometer Control** window.
By connecting with the spectrometer in this list, you can perform NMR measurement.

■ Connecting to spectrometer

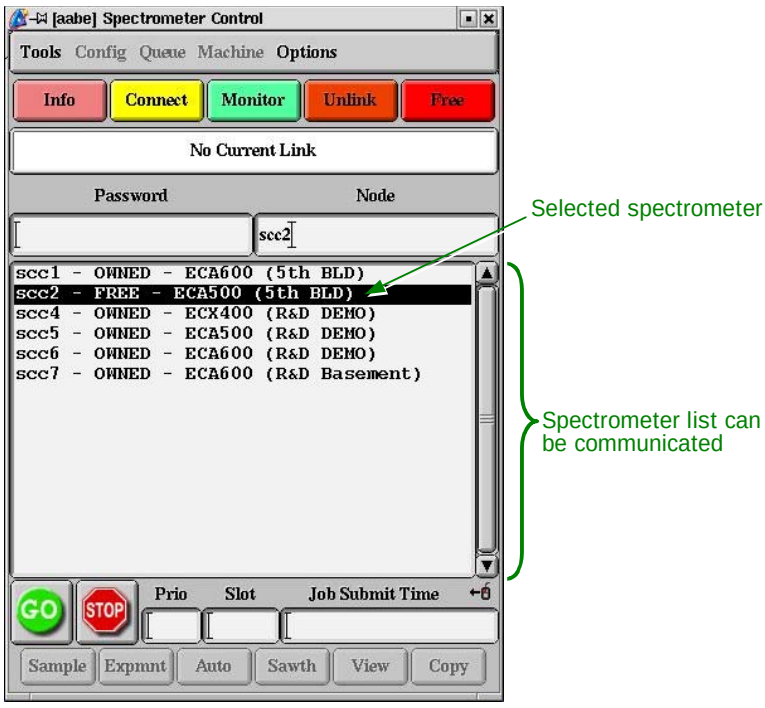
There are three ways to connect to the spectrometer.
When performing out NMR measurement, connect in the **Connect** mode.

✍ Connection is restricted by the account logged into.
Refer to the "ADMINISTRATOR'S MANUAL" for these setting.

✍ Even if you have the right to connect, connection in a specified mode may not be performed according to the state of the spectrometer.

Mode	Explanation
Monitor	Monitors the state and measurement conditions of the spectrometer. When other users have already connected with spectrometer, only Monitor mode may be connected. NMR measurement cannot be performed. However, measurement can be reserved. Measurement can be started when anyone who has connected in Connect mode releases the spectrometer.
Connect	NMR measurement and spectrometer control are performed in this mode.
Console	In this mode, deleting the jobs records to the Queue from other work stations, forced release of spectrometer connection from other work stations, change in a job priority, and rewriting of system files can be performed. However, NMR measurement cannot be performed.

1. Select the target spectrometer using the mouse from the spectrometer list displayed in the **Spectrometer Control** window and can be communicated.
Selection highlights the name of the selected spectrometer.


[aabe] Spectrometer Control
Tools Config Queue Machine Options
Info Connect Monitor Unlink Free
No Current Link
Password Node
scc2
scc1 - OWNED - ECA600 (5th BLD)
scc2 - FREE - ECA500 (5th BLD)
scc4 - OWNED - ECX400 (R&D DEMO)
scc5 - OWNED - ECA500 (R&D DEMO)
scc6 - OWNED - ECA600 (R&D DEMO)
scc7 - OWNED - ECA600 (R&D Basement)
GO
STOP
Prio Slot Job Submit Time
Sample Expmnt Auto Sawth View Copy
Selected spectrometer
Spectrometer list can be communicated

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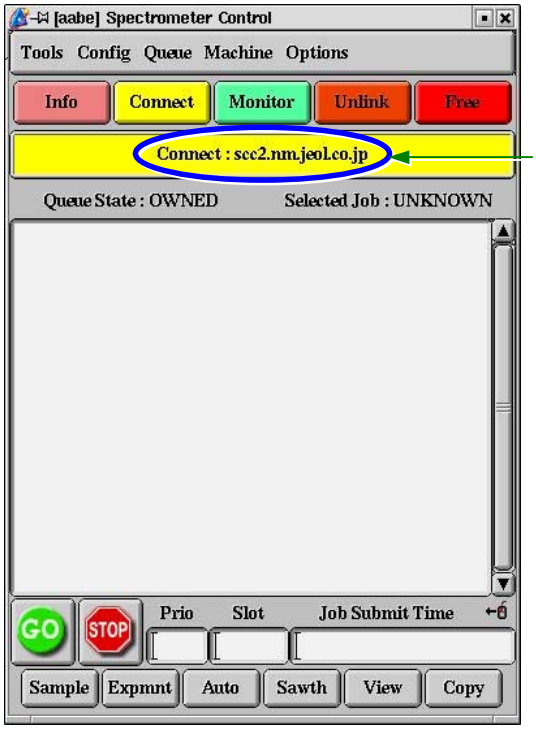
2. Click on the **Connect** button.



Node name of connection mode and connection place appear.

If status display of the selected spectrometer is not **Free**, it cannot be connected in the **Connect** mode. It is connected automatically in **Monitor** mode.

C I

Release of a spectrometer

◆ Click on the **Unlink** button of the **Spectrometer Control** window.

Connection with a spectrometer is released and a connectable spectrometer is displayed.

Confirming spectrometer information

The information on a spectrometer to connect or on the connected spectrometer can be verified using the following procedures.

Information of a spectrometer to connect

1. Select the spectrometer to connect in the **Spectrometer Control** window using the mouse.
   The name of the selected spectrometer is highlighted.
2. Click on the **Info** button.
   The **Info** window opens.

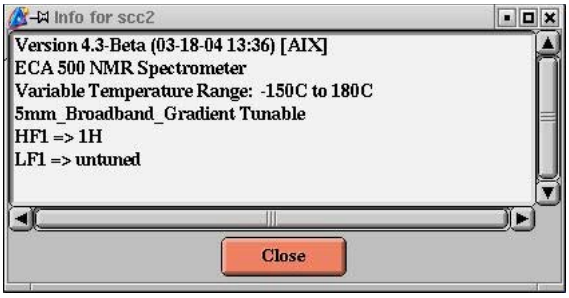


Fig. 2.2 Info window (before connection)

The kind of spectrometer, magnetic field strength, information appearing in machine.info for this spectrometer, and its probe information are displayed.

Information of on the connected spectrometer

- Click on the **Info** button in the **Spectrometer Control** window.
  The **Info** window opens.

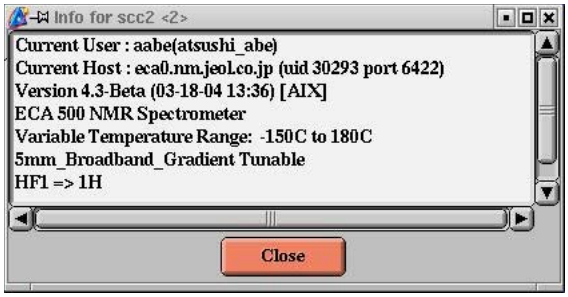

Info for scc2 <2>
Current User : aabe(atsushi_abe)
Current Host : eca0.nm.jeol.co.jp (uid 30293 port 6422)
Version 4.3-Beta (03-18-04 13:36) [AIX]
ECA 500 NMR Spectrometer
Variable Temperature Range: -150C to 180C
5mm_Broadband_Gradient Tunable
HF1 => 1H
Close

Fig. 2.3 Info window (after connection)

In addition to the information before connection, user information and information on the connected workstation is displayed.

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Display of the available spectrometer

◆ Click on the **Free** button in the **Spectrometer Control** window.

The node name and user for all available spectrometers on a network are investigated and displayed.

Connection is also canceled at this time.

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2.1.3 Management of the Measurement Queue

In the **Spectrometer Control** window, the Queue measurement can be managed.

■ Starting measurement Queue

This is the starting method for the measurement Queue in the hold state.

◆ Click on the **Go** button in the **Spectrometer Control** window.
Measurement Queue starts in the Hold state.

✍ In normal measurement, if you click on the **Submit** button in the **Experiment Tool** window, since the measurement Queue starts automatically, it is not necessary to start the measurement Queue by the **Go** button.

■ Canceling measurement Queue

This is the canceling method of measurement Queue.

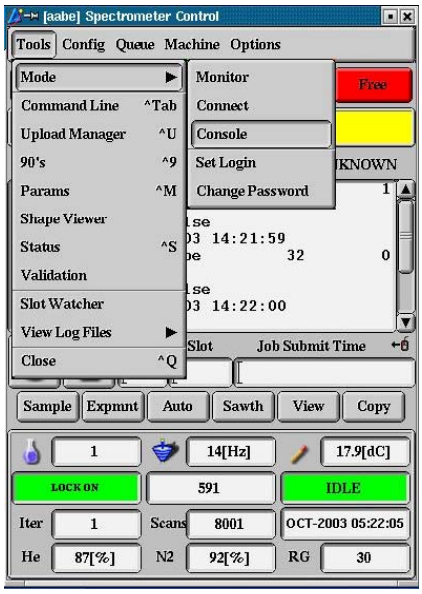
1. Select the measurement queue to cancel from the measurement Queue list box displayed by the mouse.
The selected measurement Queue is highlighted.

2. Click on the **STOP** button in the **Spectrometer Control** window.
The selected measurement Queue is canceled.

■ Changing Queue priority

Changing the priority value attached to each Queue can change the Queuing order. The priority value is 0 to 255. Higher priority carries a greater value. The default priority is 32.

1. Change the connection mode to **Console** mode.



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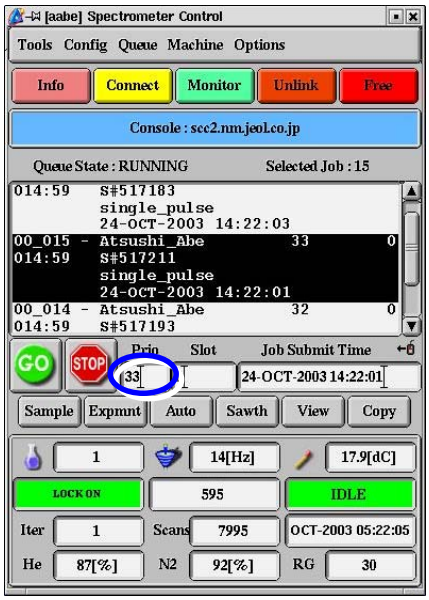
2. Select Queue to change the priority.

3. Change the priority value.



Measurement Queue order is changed when priority value is changed.

2.1.4 Sample Monitor

The state of the present sample can be displayed in the **Spectrometer Control** window.

- In the menu bar of the **Spectrometer Control** window, select **Options**–**Monitor Params**, and turn ON the toggle switch.

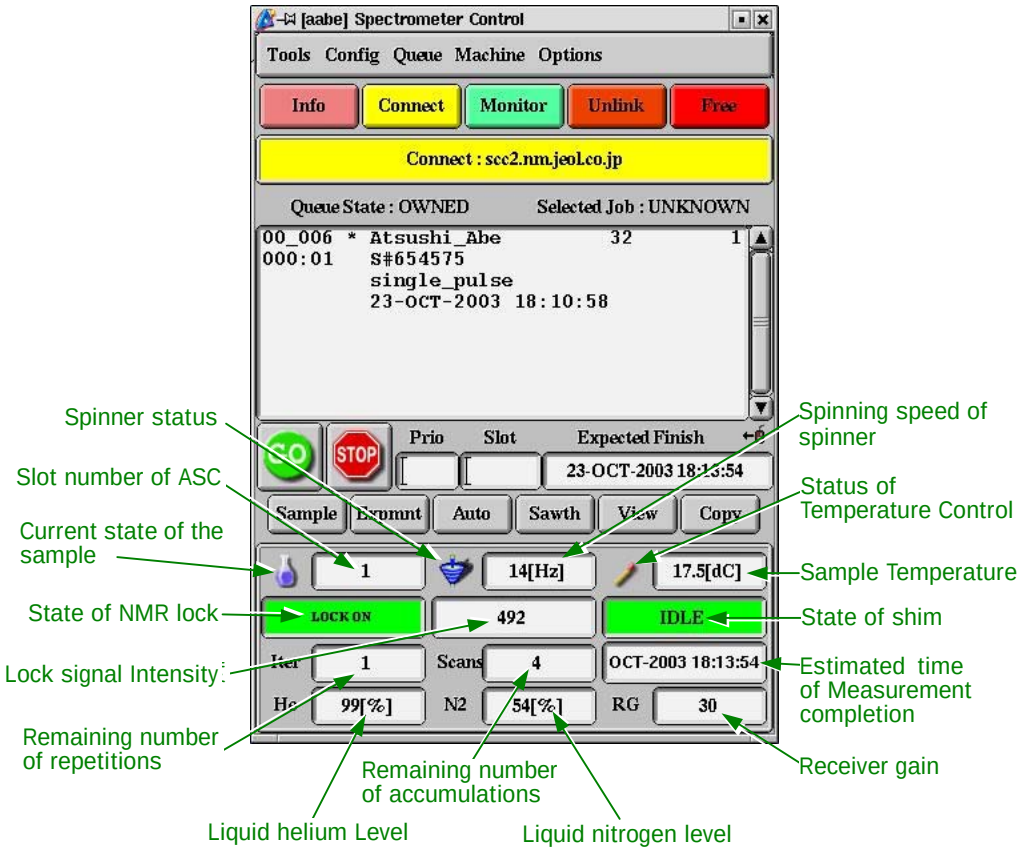


Fig. 2.4 Sample monitor in the Spectrometer Control window

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2.2 SAMPLE TOOL WINDOW

In the **Sample Tool** window, loading a sample, spinning, NMR lock, and shim adjustment can be performed.
The main information displayed in the **Sample Tool** window is as follows:

Items	Explanation
Field Strength	Magnetic-field-strength [T] (Display only)
Helium	Liquid helium level [%] (Display only)
Nitrogen	Liquid nitrogen level [%] (Display only)
Sample State	Sample state (Load/Eject)
Spinner	Sample Spinning state (Spin/No spin) and spinning speed [Hz]
Temperature	Variable temperature state (ON/OFF)
Solvent	Deuterated solvent name
Lock Control	NMR lock condition (Gain/Level/Phase/Offset)
Shim Control	Lock signal intensity (display only) and shim conditions

2.2.1 Starting the Sample Tool Window

- Click on the **Sample** button in the **Spectrometer Control** window.

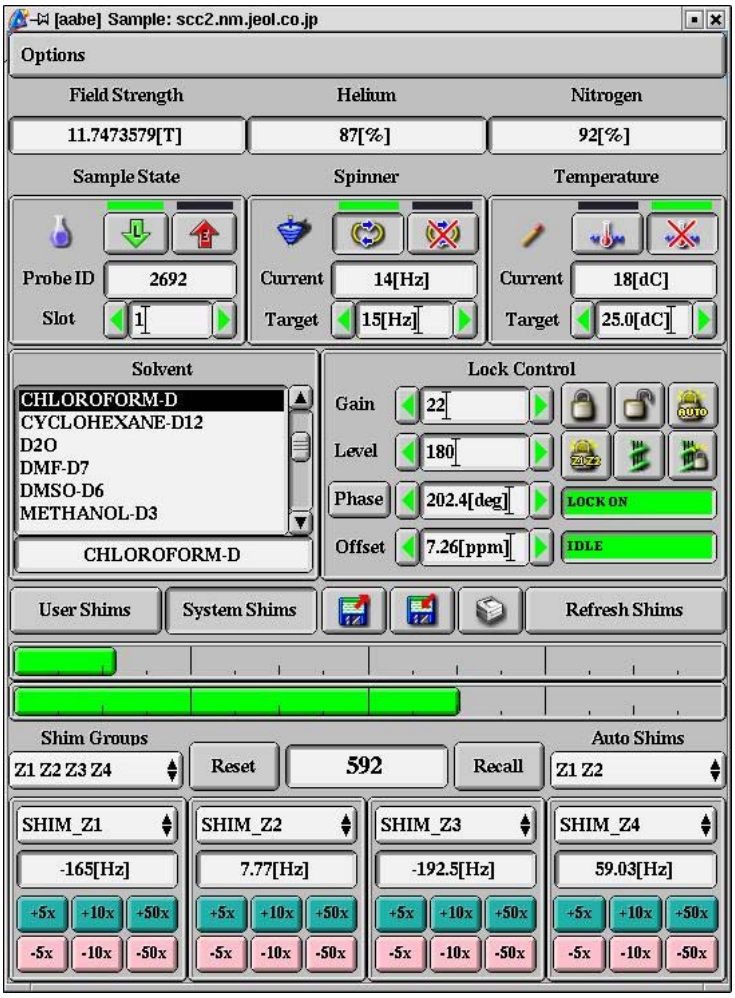

Fig. 2.5 Sample Tool window

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2.2.2 Display of SCM Related Information

Magnetic field strength

The value of this magnetic field strength is only displayed. It cannot be changed in the **Sample Tool** window.

The magnetic field strength provides very important information. NMR frequency can be calculated from the magnetic field strength and a gyromagnetic ratio (γ ratio).

The frequency offset of 0 ppm is calculated so that it may become the precise reference point (this is TMS for the ^{1}H and ^{13}C nuclei) of the scale. Using this method, any nuclei can perform criterion setting of an axis using an absolute frequency. However, change of the magnetic susceptibility of a sample produces an error. In this case, the reference position of an axis is set up using an internal standard.

Fig. 2.6 Field Strength

Liquid-helium level

The value of this liquid-helium level is only displayed. It cannot be changed in the **Sample Tool** window.

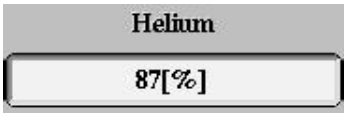

Fig. 2.7 Liquid-helium level

If it falls below the required amount, cautions (the background color of the screen turns yellow), and warnings (the background color of screen turns red) will be indicated.

Liquid-nitrogen level

The value of this liquid-nitrogen level is only displayed. It cannot change in the **Sample Tool** window.

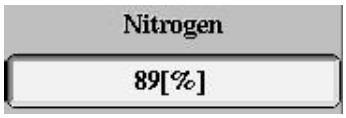

Fig. 2.8 Liquid-nitrogen level

If it falls below the required amount, cautions (the background color of the screen turns yellow), and warnings (the background color of the screen turns red) will be indicated.

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2.2.3 Loading and Ejecting a Sample

■ Sample state

The Load/Eject state of the present sample can be confirmed in display of the **Sample State** in the **Sample Tool** window.

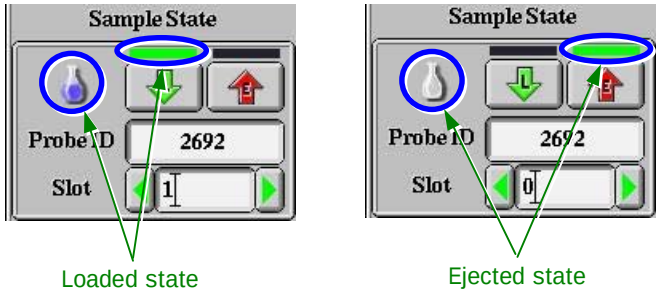

Fig. 2.9 Sample State display

✍ When the greener indicator turns yellow, this means changing from eject to load state or eject from load state is shown.

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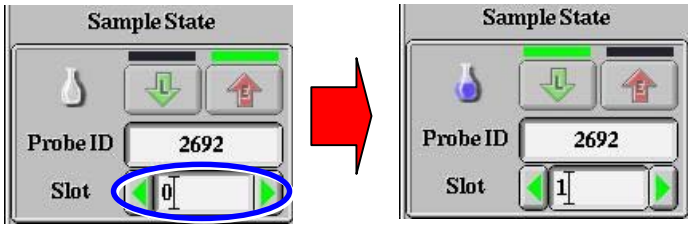
Loading a sample

When using the auto sample changer

When using the auto sample changer, a series of steps from changing to loading a sample can be performed simply by automatically setting a slot number.

◆ Enter the slot number to set a sample on the auto sample changer in a **Slot** in the **Sample State** of the **Sample Tool** window.

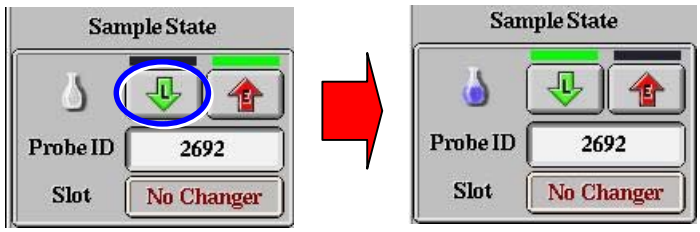


After carrying the sample in the slot that specified on the auto sample changer, on SCM, it is loaded and the sample state changes to load state.

In order to prevent trouble during loading and ejecting a sample by the auto sample changer, set **Spectrometer Load/Eject Disable** in the **System** tab of the **Preferences Tool** window to **TRUE**. The load and eject button of a sample are dimmed in this way, and to prevent mistake in operation.

When not using the auto sample changer

◆ Click on the button in the **Sample State** of the **Sample Tool** window.



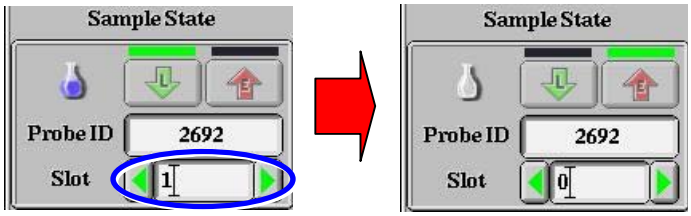
A sample is loaded, and the sample state changes into the load state.

Ejecting a sample

When using the auto sample changer

When using the auto sample changer, a series of work from ejecting to changing the sample can be performed simply setting a slot number.

◆ Enter the slot number 0 in the **Slot** in the **Sample State** of the **Sample Tool** window.

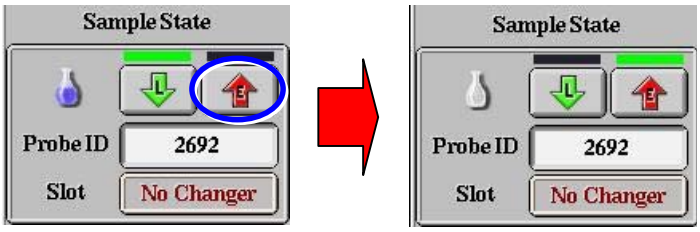


The sample is ejected and carried on an auto sample changer. The sample state changes to eject state.

In order to prevent the trouble at the time of loading and ejection by the auto sample changer, set **Spectrometer Load/Eject Disable** in the **System** tab of the **Preferences Tool** window to **TRUE**. The load and eject button of a sample are dimmed by this operation, and this can prevent mistake in operation.

When not using an auto sample changer

◆ Click on the button in **Sample State** of the **Sample Tool** window.



A sample is ejected, and the sample state changes into the eject state.

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2.2.4 Sample Spinning

■ Spinning state

Load/eject state of the present sample can be verified in the display of a **Sample State** in the **Sample Tool** window.

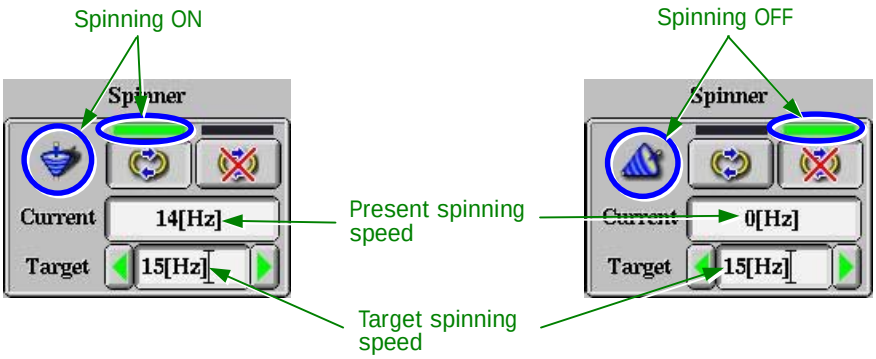
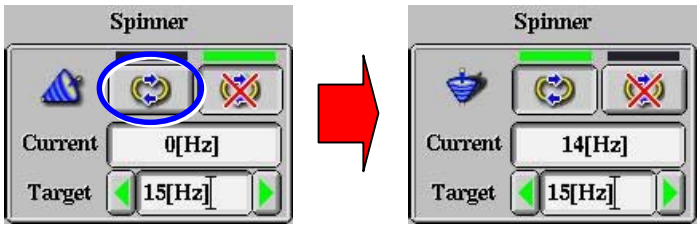


Fig. 2.10 Spinner display

When the green indicator turns yellow, this means changing from the spin-off state to the spin on state or the spin-off state from the spin on state.

■ Spinner on

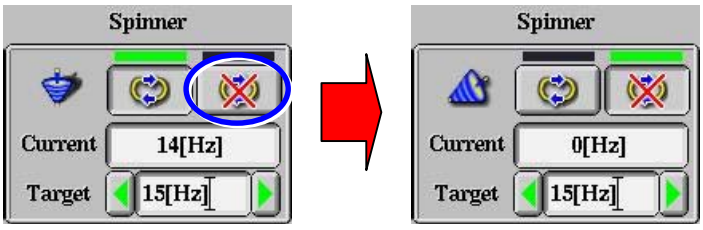
◆ Click on the button in the **Spinner** of the **Sample Tool** window.



A sample begins a spinning and the sample state changes into the spin on state.

■ Spinner off

◆ Click on the button in the **Spinner** of the **Sample Tool** window.



A sample is ejected, and the sample state changes into the eject state.

2.2.5 Variable Temperature (VT)

■ Sample temperature

The temperature control state of the sample can be verified by **Temperature** display in the **Sample Tool** window.

● When the Temperature Hold function is not provided

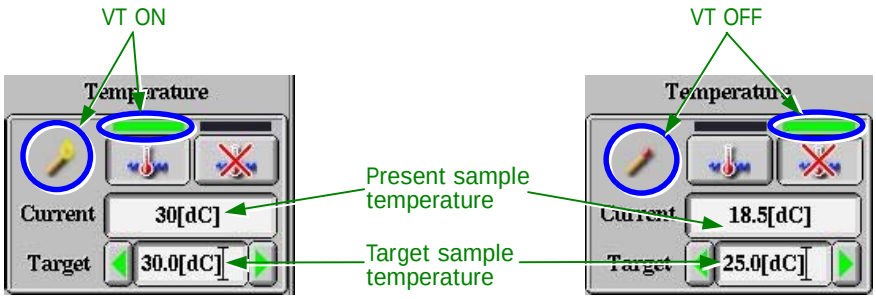


Fig. 2.11 Temperature display (without the Temperature Hold function)

✍ When the green indicator turns yellow, this indicates to change from VT OFF state to VT ON state or VT OFF state from VT ON state is shown.

● When the Temperature hold function is provided

✍ In order to use temperature hold function, after changing the value of TEMP_HOLD _AVAILABLE in the machine.config file of the spectrometer into TRUE, it is necessary to restart the spectrometer.

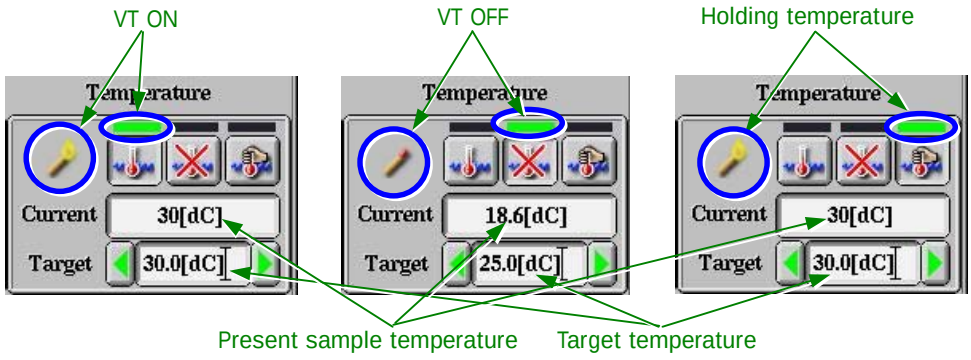


Fig. 2.12 Temperature display (with the Temperature Hold functional)

✍ When the green indicator turns yellow, this shows to change from the present VT OFF state to VT ON state or VT OFF state from VT ON state.

✍ The temperature in a temperature hold is the temperature of the sample space (this means holding this temperature during a sample exchange).

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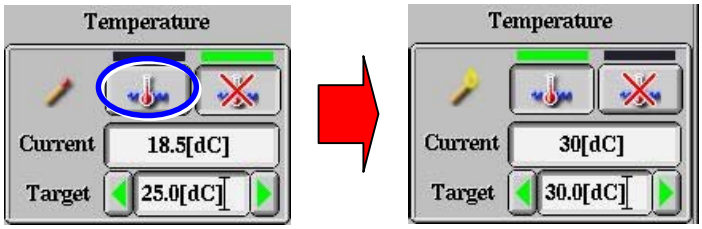
VT ON

When the temperature hold function is not provided

◆ Click on the button under **Temperature** in the **Sample Tool** window.

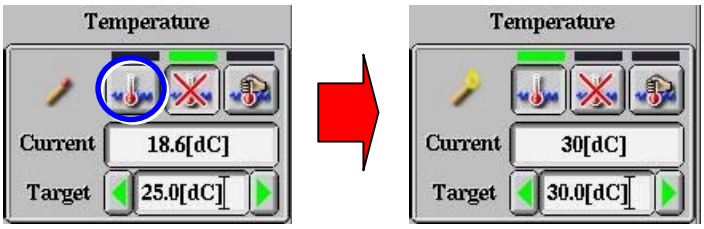


The temperature controller begins operation, and the state display of a sample changes to the VT ON state.

When setting the temperature-exceeding boiling point and melting point of the selected solvent to **Target**, a warning display appears, and the temperature setting is reset.

When the temperature hold function is provided

◆ Click on the button under **Temperature** in the **Sample Tool** window.

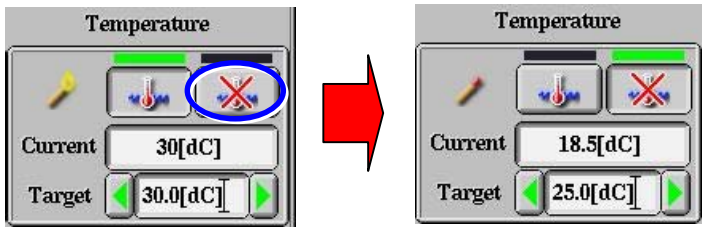


The temperature controller begins operation, and the state display of a sample changes into the VT ON state.

When setting the temperature exceeding boiling point and melting point of the selected solvent to **Targe**t, a warning display appears, and the temperature setting is reset.

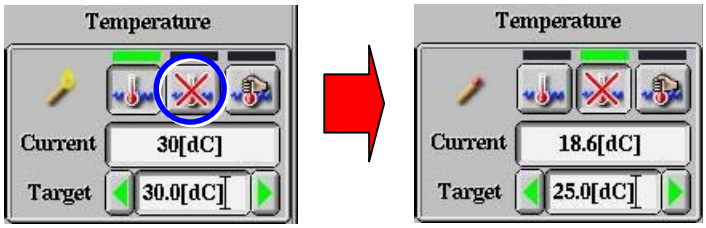
VT OFF

- **When the temperature hold function is not provided**
  - Click on the button in **Temperature** of the **Sample Tool** window.



The temperature controller stops, and the state display of a sample changes to the VT OFF state.

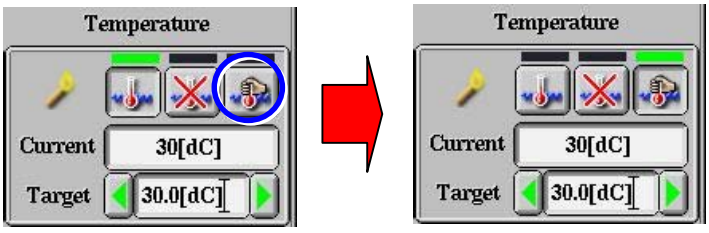
- **When the temperature hold function is provided.**
  - Click on the button in **Temperature** of the **Sample Tool** window.



The temperature controller stops, and the sample state changes into the VT OFF state.

Temperature Hold

- Click on the button under **Temperature** in the **Sample Tool** window.



In this the temperature hold mode, and sample exchange can be performed with the state of VT ON.

In order to prevent damage by fire from a heater, if you cannot terminate sample exchange during a fixed time, VT is turned off automatically.

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2.2.6 Selecting the Deuterated Solvent

Select a deuterated solvent of a sample from the **Solvent** list box. The following example shows that **CHLOROFORM-D** has been selected.
If you make mistake in this setting, the NMR lock not only cannot be applied, but reference setting will not be performed correctly.

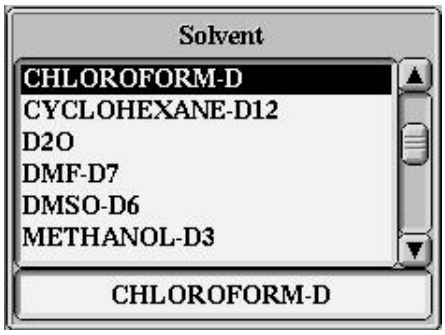

Fig. 2.13 Solvent list box

When selecting an item from the list box, it is convenient to use the skip function. If you move the mouse pointer into the list box, and enter the first character of an item name from the keyboard, it will skip automatically to the position of the target item. For example, if C (a capital letter) is entered from the keyboard when the mouse pointer is in the **Solvent** list box, it will skip to **CHLOROFORM-D**.

2.2.7 Control the NMR Lock

The NMR lock is controlled in **the Lock Control** part of the **Sample Tool** window.

Fig. 2.14 Lock Control

In the NMR lock a system, in order to retain the magnetic field stability, the magnetic field is locked using NMR signal of ^{2}H nucleus in the sample. If the magnetic field is changed or drifts, the magnetic field will be stabilized using the Z0 axis shim coil. Moreover, the lock signal intensity is used for shim adjustment. The intensity of a signal becomes strong so that the magnetic field is uniform.

When using the NMR lock system, the ^{2}H nucleus must be contained in the sample. Usually, the ^{2}H nucleus exists in the deuterated solvent, such as Chloroform-d, Benzene-d6, and Acetone-d6.

Measurement is performed without applying the NMR lock for the sample in which the ^{2}H nucleus is not contained. Moreover, when measuring the ^{2}H nucleus, measurement is performed using the mode without the NMR lock.

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NMR Lock Control Button

Click the following button in **Lock Control** to control the NMR lock.

Icon	Function	Explanation
	Lock ON	The NMR lock is turned on to the ^{2}H signal included in sample. Wide range search of a lock signal is not performed. Therefore, it is necessary to adjust Z0 in the Sawtooth window so that a lock signal may adjust in advance to the position of lock frequency.
	Lock OFF	NMR lock is turned off. However, since the output of the lock oscillator does not stop, in addition to Lock OFF instruction, it is necessary to change an instrument parameter LOCK OSC STATE to ^{2}H OSC OFF when observing a ^{2}H nucleus. Refer to the **Parameter Tool** for changing instrument parameters.
	Auto Lock	Wide range search of the lock signal is carried out, and if a signal is found, the NMR lock will be turned on. Moreover, the level and gain of the NMR lock will be adjusted automatically.
	Auto Lock&Shim	The Z1 axis and Z2 axis shim is adjusted automatically after automatical locking.
	Gradient Shim	Shimming is performed by gradient shim. The execution conditions of the gradient shim are described in gradient_solvent2 file of the instrument directory.
	Gradient Shim&Lock	Automatically locking is performed after performing the gradient shimming.
	Optimize Lock Phase	The lock signal phase is optimized. In order to use this function, it is necessary to turn on the NMR lock in advance.

NMR lock relation parameter

Parameter	Explanation
NMR lock state (only display)	The NMR lock state at present is displayed. Red is lock-off, yellow is during the search for the lock signal, and green is lock-on.
Gain	This is a gain of the lock receiver. The amplification rate of a lock signal is adjusted. Usually, the value described in the solvent.def file is set up. In case of an auto lock, a gain is adjusted automatically and NMR lock signal is detected.
Level	This is the output level of the lock channel. Usually, the value described in the solvent.def file is set up. In case of an auto lock, the level is adjusted automatically and an NMR lock signal is detected.
Phase	This is the lock signal phase. The value described in the shim file is set up. A lock phase depends on RF filter in the mainly used probe and the lock channel. Moreover, if the dielectric constant of a sample and an ion concentration changes greatly, the lock phase may change.
Offset	This is the offset lock frequency. Usually, the value described in the solvent.def file is set up. It is the frequency offset required in order to set TMS as to 0 ppm.

2.2.8 Shim Control

The **Sample Tool** window controls shimming. In the **Sample Tool** window, a shim of four axes is displayed as one group (a shim group). In order to change a display group, select the shim group to display from the **Shim Groups** list box, or select it from the list box in the display shim axis.

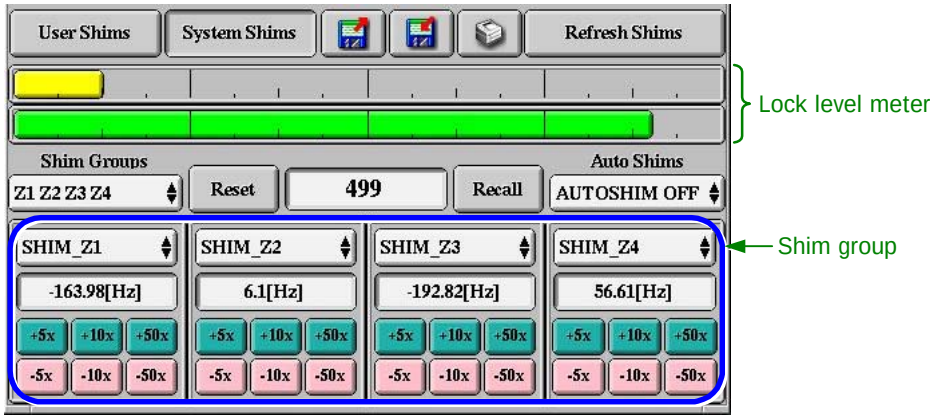

Fig. 2.15 Shim control part

Each shim value can be saved as a shim file. The shim value can be read from the file and used it if necessary.

In the shim file, there are two kinds of shim for a system shim and a user shim. One system shim exists per probe. Moreover, this system shim is saved in the spectrometer ; anyone can read this shim value. However, only administrator can rewrite the system shim.

On the other hand, a user can create a user shim for every measurement conditions, such as a probe, a sample, or a solvent. A user shim is saved to a user's local directory.

■ Saving shim value

● Saving to the user shim file

1. Click on the User Shims button in the **Sample Tool.**
2. Click on the button.

   The **Save Shim File** window opens.

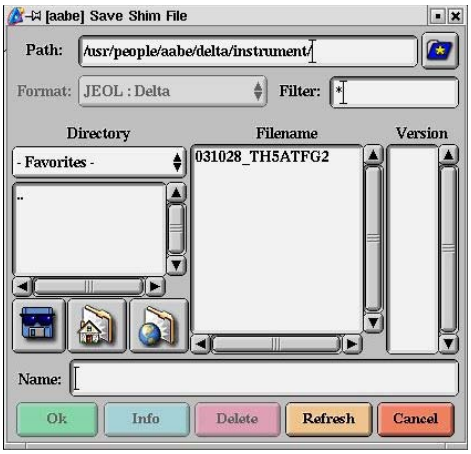

Fig. 2.16 Save Shim File window

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3. After moving to the directory to save, input file name to save to the **Name** input box, and click on the **Ok** button.

The shim value is saved to a user shim file.

When creating a new directory to save to, click on the button after specifying a directory name to the **Path** input box. Create and transfer a directory. Then, input a saving file name into the file name input box.

- **Saving to the system shim file**

1. Select **Tools**–**Mode**–**Console** in the **Spectrometer Control** window.

This becomes Console mode.

Work is done by the user with administrator privilege, who user's right to Console mode.

2. Click on the System Shims button in the **Sample Tool.**

3. Click on the button.

The **Confirm** window opens.

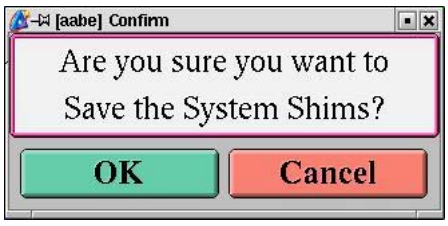

Fig. 2.17 Confirm window

4. Click on the **Ok** button when saving a system shim file.

The shim value is saved to a system shim file.

Reading a shim file

Reading a system shim file

1. Click on the System Shims button in the **Sample Tool.**
2. Click on the button.
   The **Confirm** window opens.

Fig. 2.18 Confirm window

3. Click on the **Ok** button when reading a system shim file.
   A system shim is loaded.

Reading a user shim file

1. Click on the User Shims button in the **Sample Tool.**
2. Click on the button.
   The **Open Shim File** window opens.

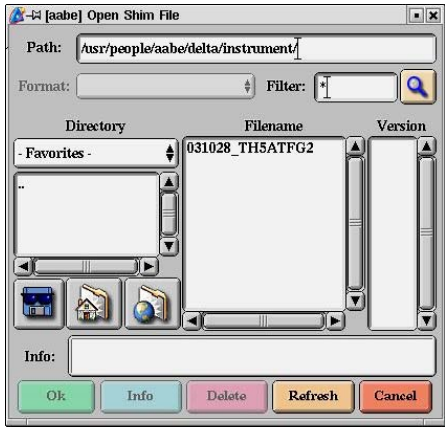

Fig. 2.19 Open Shim File window

3. Select a shim file name to read with the mouse, and click on the **Ok** button.
   The shim file is read and the shim value is set to each axis. Information of the read shim file appears on the **Inform** window.

Fig. 2.20 Inform window

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Shim control button and list box

The followings button and list box are used for controlling shims.

Button	Explanation
Reset	The spectrometer is always monitoring shim value and lock signal intensity, It has memorized the best shim value at maximum lock signal intensity. This best shim value is cleared.
Recall	The best shim value is called and the value is set to each axis.
Refresh Shims	The shim value displayed on the **Shim Control** part in **Sample Tool** is updated to the shim value set to the spectrometer now.
Auto Shims AUTOSHIM OFF	Automatic shim adjustment of the specified axis is performed. When performing automatic shim adjustment, select the combination of an axes to perform automatic shim adjustment from the list box. If selection is complete, automatic shim adjustment will start. Select AUTOSHIM OFF when you want to stop automatic shim adjustment.

Shim-control relation parameters

Lock signal display

The bar graph in the top of **the Shim Control** part is called a “lock level meter”. This is used to monitor the lock signal intensity. The upper of the bar graph is “Coarse” and the lower is “Fine”. Moreover, the actual lock signal intensity is also displayed numerically.

Fig. 2.21 Lock level meter

2.3 EXPERIMENT EDITOR TOOL WINDOW

If you click on the **Expmnt** button in the **Spectrometer Control** window, the **Open Experiment** window that selects a pulse sequence opens. Then, if you select a pulse sequence, and click on the **Ok** button, the **Experiment Tool** window that sets a measurement parameter will also open.

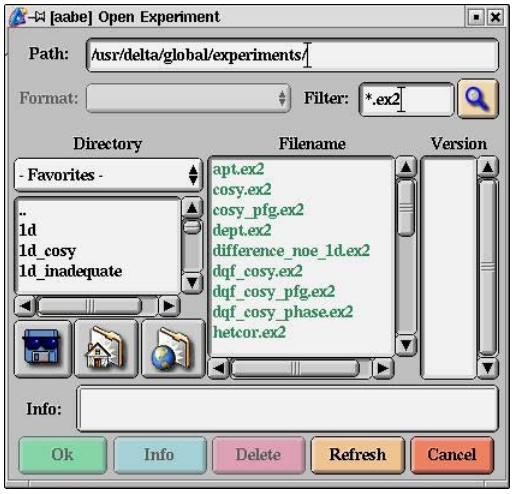

Fig. 2.22 Open Experiment window

If you select a pulse sequence in the **Open Experiment** window, and click on the Ok button, the **Experiment Tool** window opens.

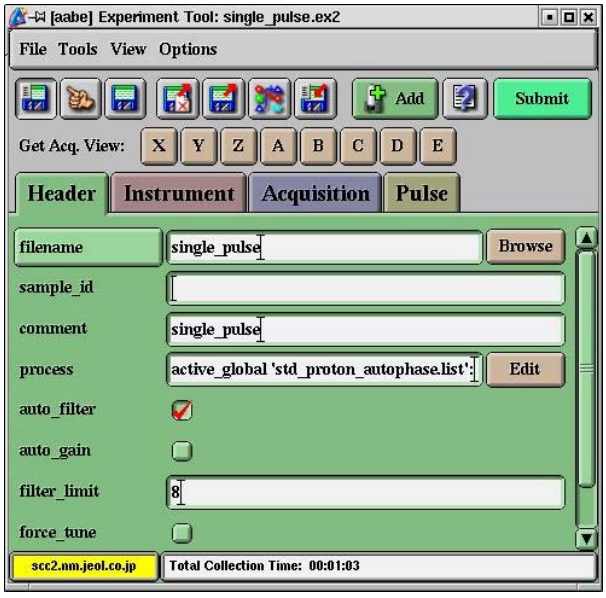

Fig. 2.23 Experiment Tool window

In **the Experiment Tool** window, the parameters foe each section **Header**, **Instrument**, **Acquisition**, and **Pulse** are set up, and measurement is started by the selecting **Submit** button.

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2.3.1 Measurement File (Experiment File)

In this spectrometer, the file in which the pulse sequence was stored is called the measurement file (Experiment File). A measurement file contains the standard value of a measurement parameter in addition to a pulse sequence.

■ Storage area for a measurement file

● Local directory

Clicking on the button in the **Open Experiment** window lists the measurement file in a local directory.
A local directory is a directory specified to **Experiment** in the **Directory** tab of the **Preferences Tool** window.
The measurement files which are user created and corrected are stored in this directory.

● Global directory

Clicking in the button in the **Open Experiment** window lists the measurement file in a global directory.
A global directory is a directory specified to **Global Experiment** in the **Directory** tab of the **Preferences Tool** window.
The measurement file of the standard, which JEOL supplies, is stored in this directory.

2.3.2 Header Section

In the **Header** section of the **Experiment Tool** window, parameters, such as **sample_id, filename**, and **comment** are set.

The **Header** section has two important functions in addition to this. One is setting a process list. It specifies which process list is to be used on the data after acquisition. Another is a header parameter. If you use this function, various spectrometer functions and data-acquisition conditions can be controlled.

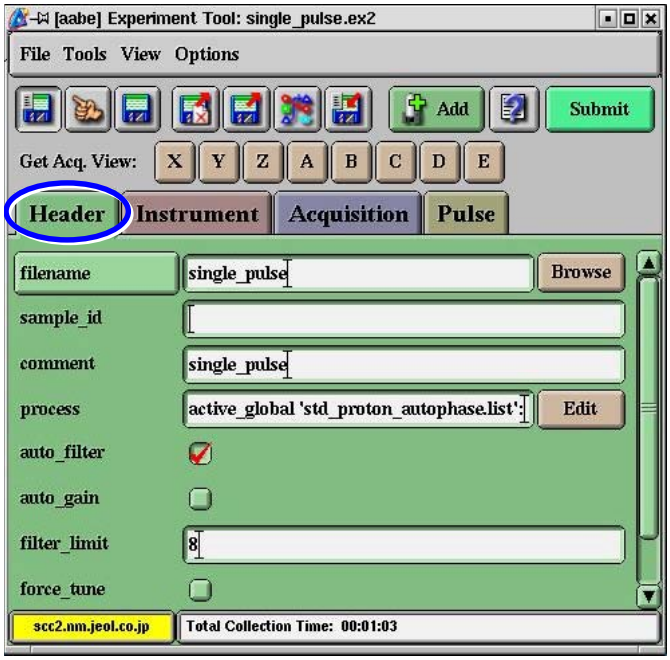

Fig. 2.24 Header section of the Experiment Tool

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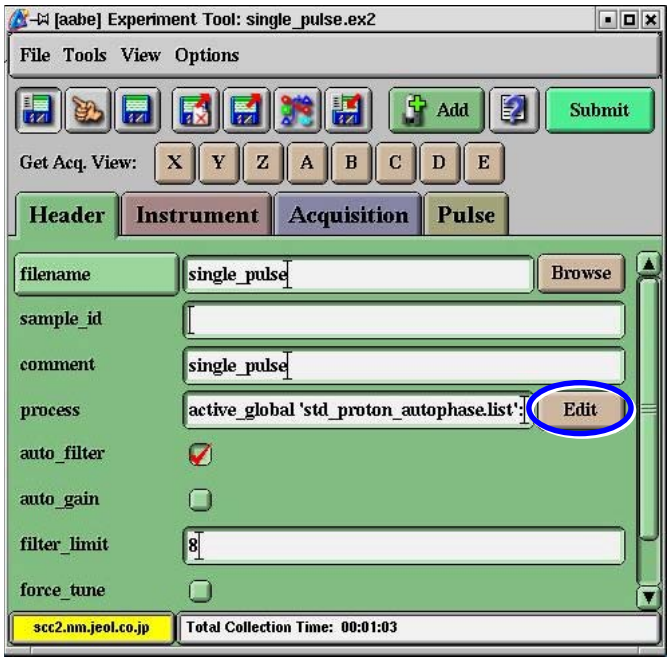
Setting process list

The default process list is described in the measurement file supplied as a standard. When changing these contents, you can change a process list in the following procedure.

1. Click on the **Edit** button in the **Header** section of the **Experiment Tool** window.



The **Set Process** window opens.

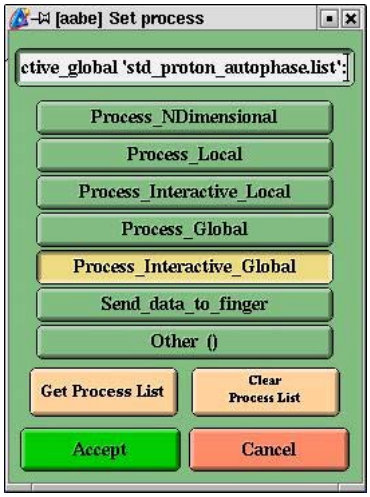


Fig. 2.25 Set Process window

2. Select the kind of process list:

Kinds	Explanation
Process_Ndimensional	The data is sent to **1D Processor** or **nD Processor** after measurement is complete. However, processing is not performed.
Process_Local	Data processing is performed using the specified process list in a local directory after a measurement is complete, and the result is saved. Neither **1D Processor** nor **nD Processor** is displayed.
Process_Interactive_Local	Data is sent to **1D Processor** or **nD Processor** after measurement is complete. Then, the specified process list is set in a local directory.
Process_Global	Data processing is performed using the specified process list in a global directory after measurement is complete, and a result is saved. **1D Processor** or **nD Processor** is not displayed.
Process_Interactive_Global	Data is sent to **1D Processor** or **nD Processor** after measurement is complete. Then, the specified process list in a global directory is set.
Send_data_to_finger	The process list of the data displayed on **1D Processor** and **nD Processor** is used.
Other()	The program which performs data processing is performed.

3. Select a process list.

If you click on the **Get Process List** button, the **Select Process List** window opens. Select a process list, and click on the **Ok** button.

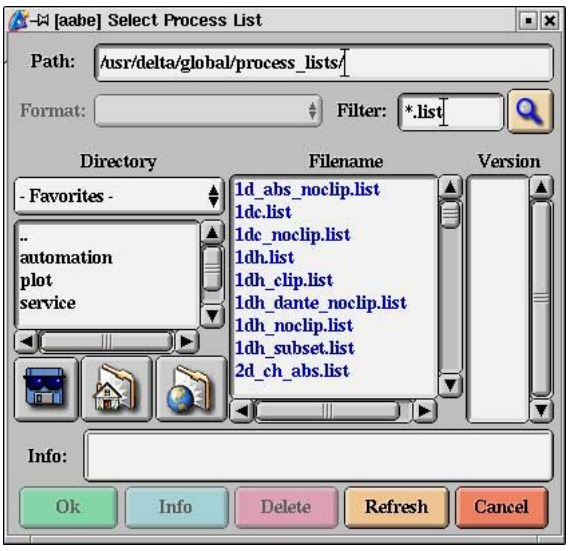


Fig. 2.26 Select Process List window

4. After setting is complete, click on the **Accept** button in the **Set Process** window.

The **Set Process** window is closed, and a new process list is set in the **process** of the **Header** section of the **Experiment Tool** window.

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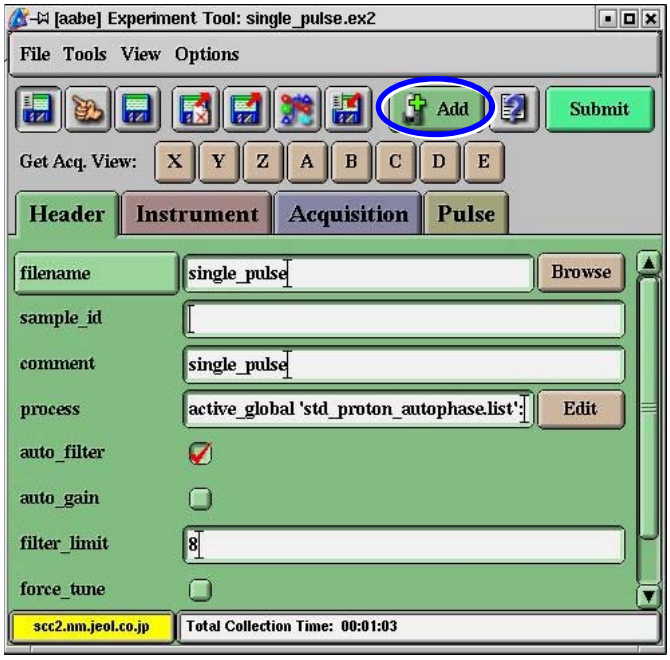
Addition of Header parameter

You can add a new parameter to the **Header** section using the following methods:

1. Click on the **Header** tab in the **Experiment Tool** window.
   The Header section appears.
2. Click on the Add button.



The **Include Parameter** window opens.

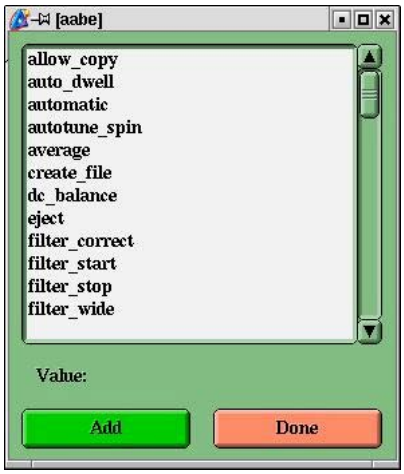


Fig. 2.27 Include Parameter window

3. Select the parameter to add.
   The selected parameter is highlighted.
4. Click on the **Add** button.
5. Repeat steps 3-4 if required.
6. Finally click on the **Done** button.
   The parameter added to the **Header** section appears.

2.3.3 Instrument Section

In the **Instrument** section, you can set the conditions of an NMR lock, receiver, and audio filter.

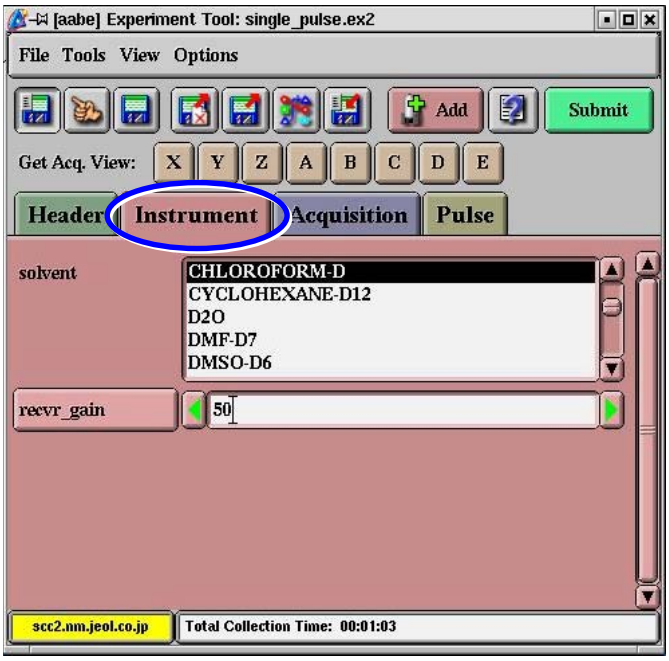


Fig. 2.28 Instrument section of the Experiment Tool

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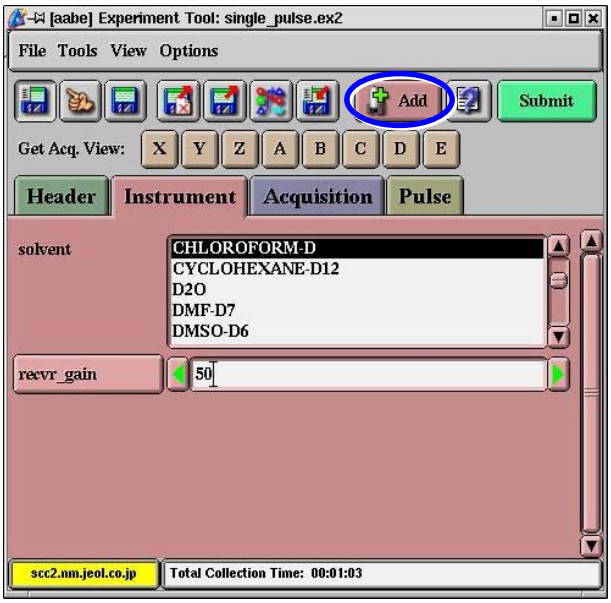
Addition of Instrument parameter

You can add a new parameter to the **Instrument** section using the following methods.

1. Click on the **Instrument** tab in the **Experiment Tool** window.
   The **Instrument** section appears.
2. Click on the Add button.



The **Include Parameter** window opens.

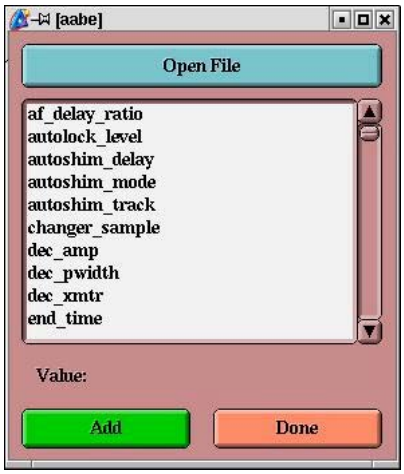


Fig. 2.29 Include Parameter window

3. Select the parameter to add.
   The selected parameter is highlighted.
4. Click on the **Add** button.
5. Repeat steps 3-4 if required.
6. Finally click on the **Done** button.
   The parameter added to **the Instrument** section appears.

2.3.4 Acquisition Section

You can set the parameters related to data acquisition (NMR observation frequency, observation width, and data point) in the **Acquisition** section.

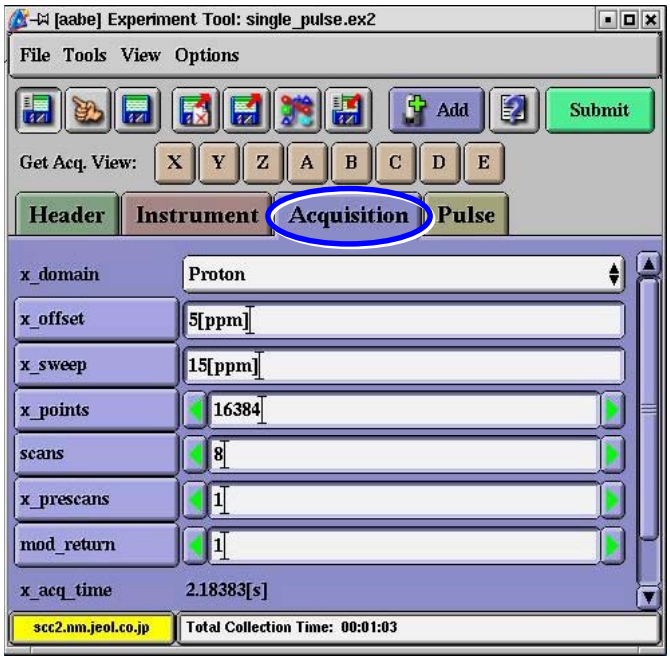


Fig. 2.30 Acquisition section of the Experiment Tool

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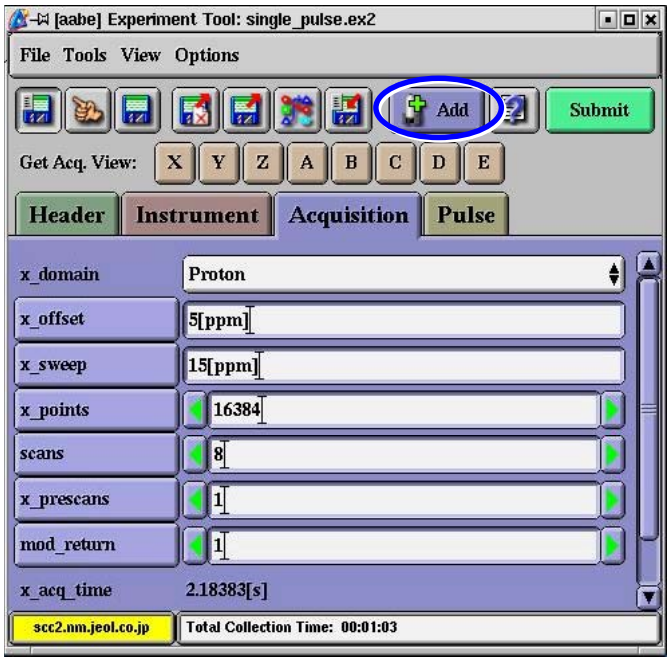
Addition of the Acquisition parameter

You can add a new parameter to the **Acquisition** section using the following methods:

1. Click on the **Acquisition** tab of the **Experiment Tool** window.
   The **Acquisition** section appears.
2. Click on the Add button.



The Include Parameter window opens.

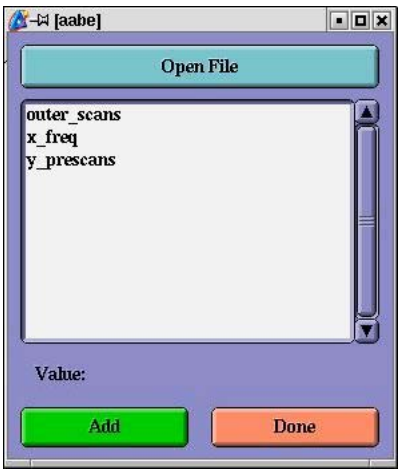


Fig. 2.31 Include Parameter window

3. Select the parameter to add.
   The selected parameter is highlighted.
4. Click on the **Add** button.
5. Repeat steps 3-4 if required.
6. Finally click on the **Done** button.
   The parameter added to the **Acquisition** section appears.

2.3.5 Pulse Section

You can set parameters, such as time and an attenuator that is required for a pulse sequence in the **Pulse** section.

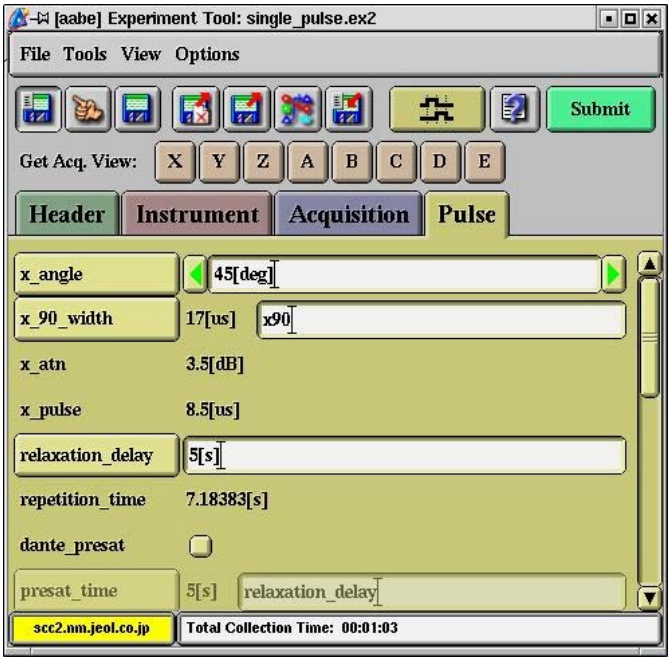


Fig. 2.32 Pulse section of the Experiment Tool

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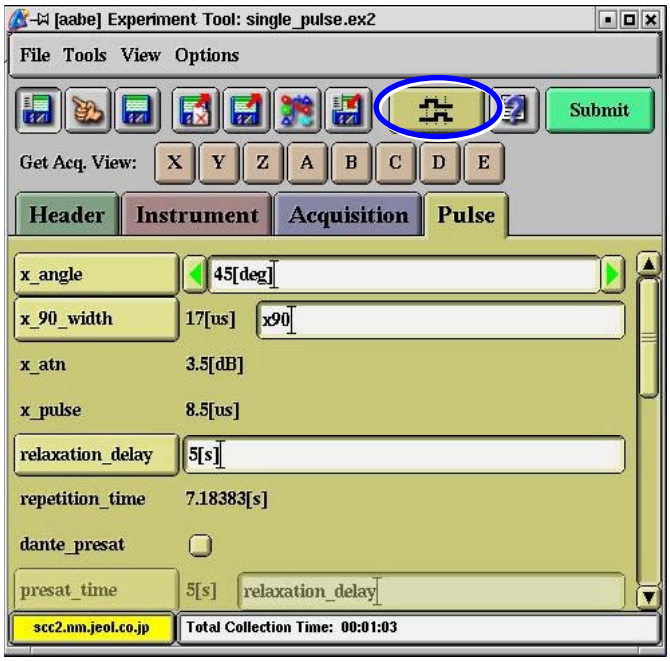
Time chart Display of pulse-sequence

You can express the time chart of a pulse sequence as the following procedure:

1. Click on the **Pulse** tab in the **Experiment Tool** window.
   The **Pulse** section appears.
2. Click on the button.



The **Pulse Viewer** window opens.

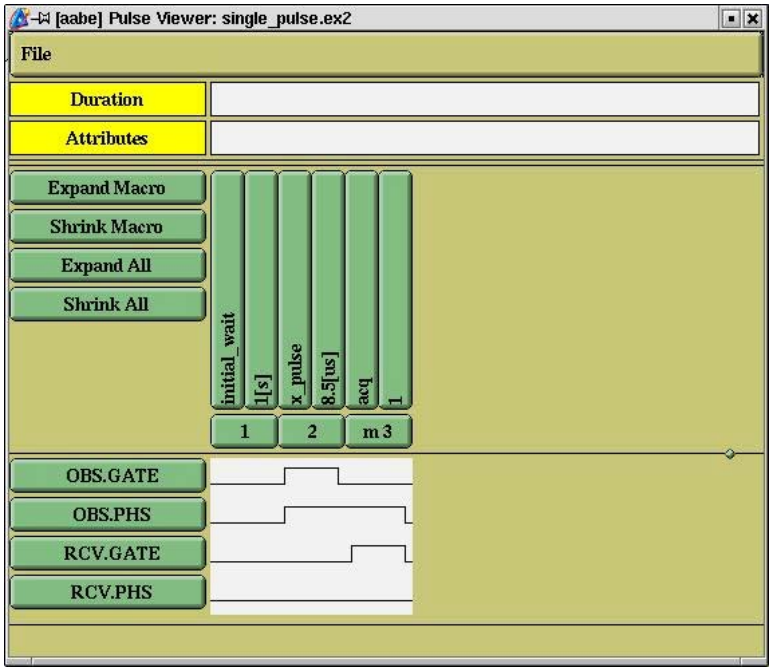


Fig. 2.33 Pulse Viewer window

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2.4 AUTOMATION TOOL WINDOW

If you click on the **Auto** button in the **Spectrometer Control** window, the **Automation** window in which all step from measurement of data to processing and printing of data are automatically performed opens.
In the **Automation** window, there are the two modes - Standard mode and Advanced mode.

☞ Refer to the “AUTOMATIC MEASUREMENT” of separate volume for details on automatic measurement.

2.4.1 Standard Mode in the Automation Window

In Standard mode, measurement is performed according to the measurement conditions of the number of scans to accumulate to repetition time as set as the default in the automatic measurement template.

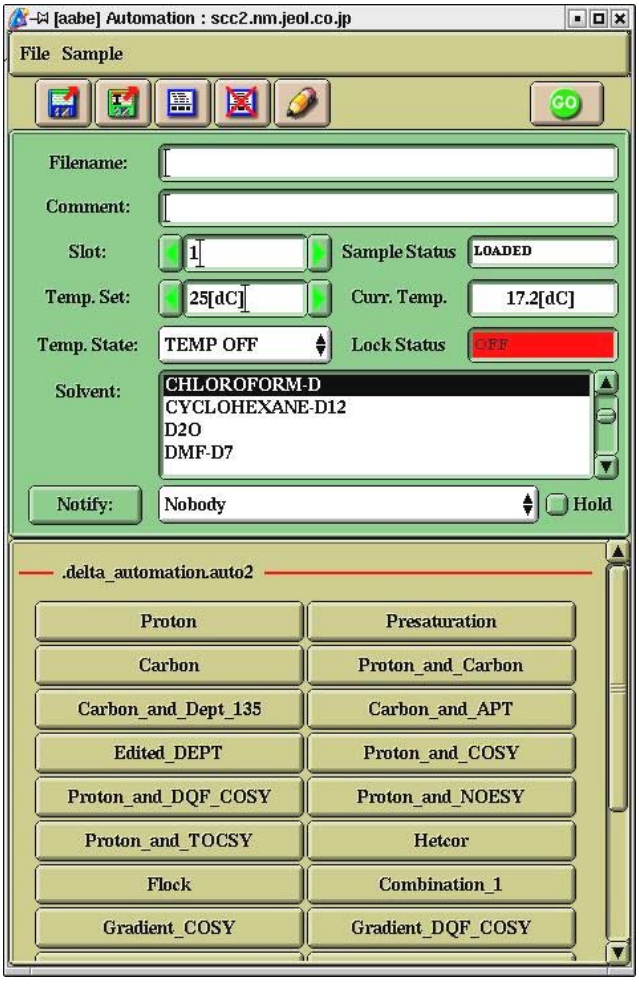

Fig. 2.34 Automation window (Standard mode)

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Start of automatic measurement

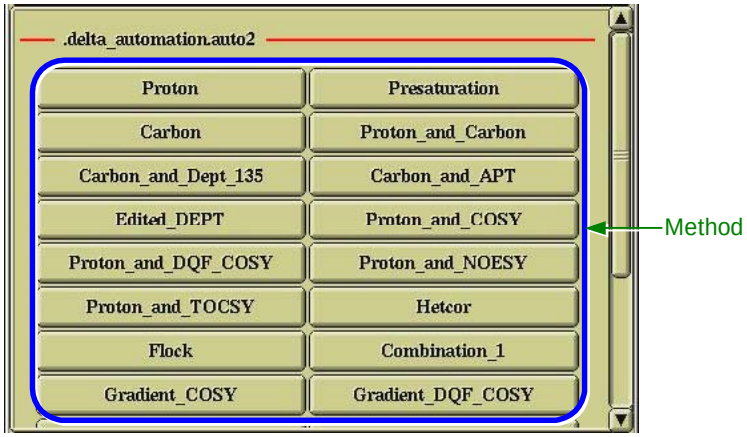
1. Enter the necessary minimal parameters in the following table:

Parameter	Explanation
Filename	Saving file name
Comment	Comment
Slot	Slot number for the auto-sample changer（at auto-sample-changer use）
Temp. Set	Setting temperature for the VT unit
Temp. State	Setting the VT state
Solvent	Solvent

2. Set up arbitrary options.

Typical arbitrary parameter	Explanation
Notify	Transmission place for the measurement completion e-mail
Hold	Holding transmission place of the measurement completion e-mail
Gradient Shim	Performing gradient shimming
Gradient Optimization	Gradient shimming is performed only when measuring the first sample or after changing the sample time.
Enhance Filename	A date is added to the file name.

3. Click on the method button.



A method can be continuously recorded like as in a measurement Queue. However, the order of measurement is the same order, recorded to the measurement Queue. If a new measurement Queue is taken from the **Experiment Tool** window during automatic measurement, it will interrupt after the Queue of the present experiment finishes.

Automation window icons

Icon	Button name	Explanation
	Open Automation File	The present automatic measurement template is deleted, and a new automatic measurement template is read.
	Include Automation File	A new automatic measurement template is added to the present automatic measurement template.
	Show Queue	The Queue display window for automatic measurement is opened.
	Hide Queue	The Queue display window for automatic measurement is closed.
	Automation Editor	The Automation Editor window is opened.
	Run Experiment	Click on this button when performing an experiment, a check window indicating when measurement is performed will appear.

Refer to the “AUTOMATIC MEASUREMENT" of a separate volume for details on automatic measurement.

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2.4.2 Advanced Mode in the Automation Window

In Advance mode, you can change measurement conditions such as number of scans to accumulate and repetition time.

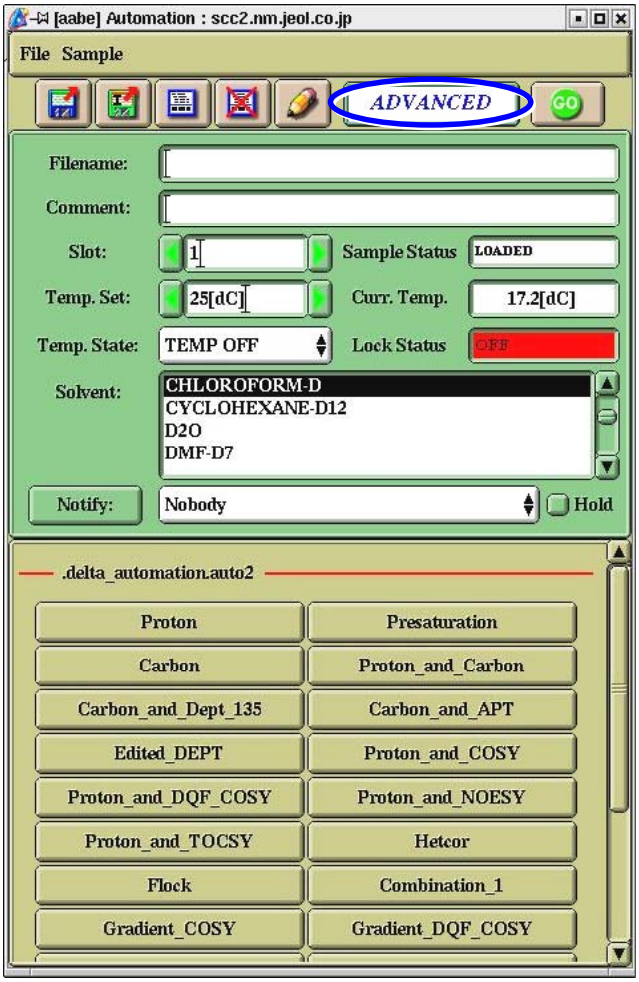
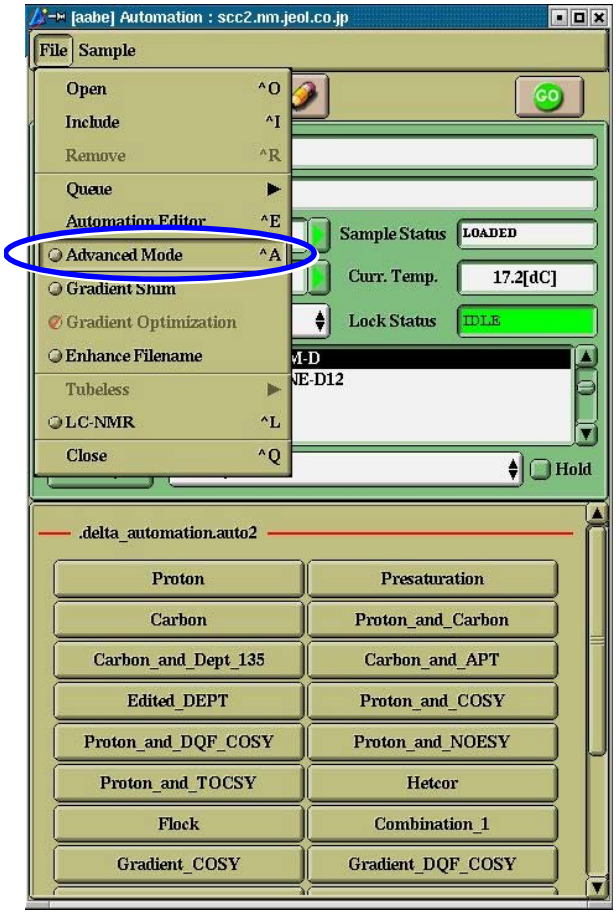


Fig. 2.35 Automation window (Advanced mode)

Change to Advanced mode

When **ADVANCED** is not displayed in the **Automation** window, Standard mode is in operation. Change to Advanced mode using the following procedures.

◆ Select **File-Advanced Mode** in the menu bar of the **Automation** window.



After changing procedure is complete, ADVANCED appears in the **Automation** window.

Starting automatic measurement

1. Enter the necessary minimal parameters in the following table:

Parameter	explanation
Filename	Saving file name
Comment	Comment
Slot	Slot number of the auto-sample changer（at auto-sample-changer use）
Temp. Set	Setting temperature of the VT unit
Temp. State	Setting VT state
Solvent	Solvent

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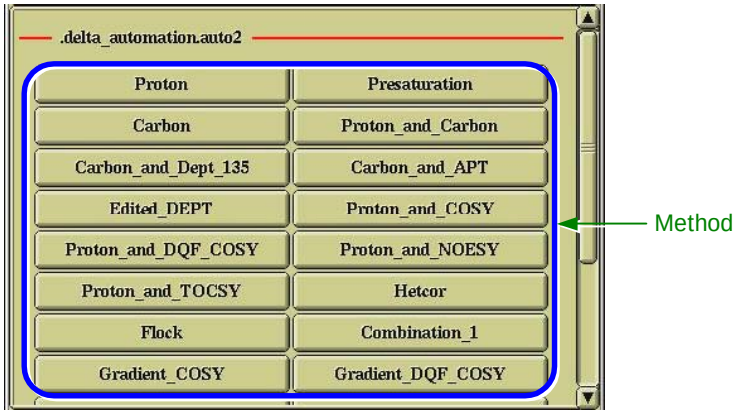
2. Set up arbitrary options.

Typical arbitrary parameter	Explanation
Notify	Transmission place for measurement completion mail
Hold	Holding transmission place for measurement completion mail
Gradient Shim	Performing gradient shimming
Gradient Optimization	A gradient shimming is performed only when measuring first sample or after changing the sample time.
Enhance Filename	A date is added to the file name.

3. Click on the method button.



The **Set Parameters** window opens.

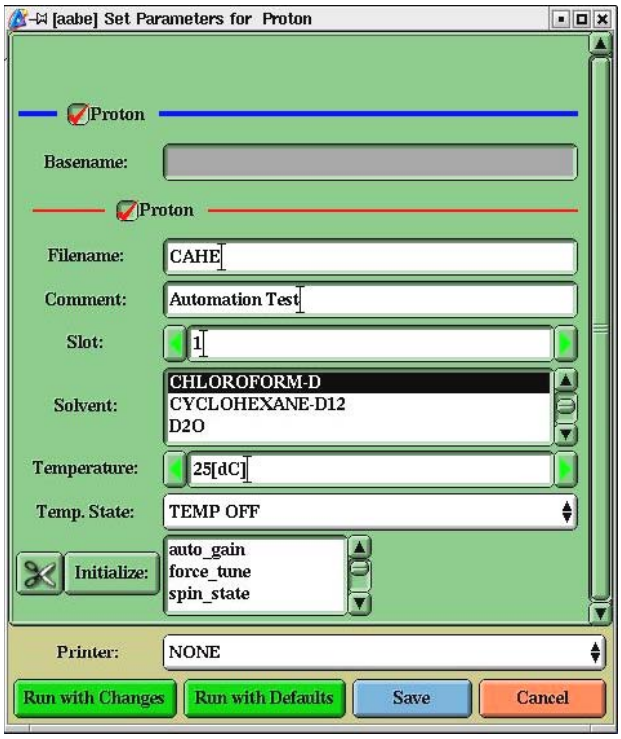


Fig. 2.36 Set Parameters window

In the **Set Parameters** window, the setting range for every group contained in the selected method exists. The range for this group is divided by a blue line.
Moreover, in the range for every group of this, the setting range for every measurement exists further. The range for this every measurement is divided by the red line.

4. Click on the button whose group name is displayed on the blue line, and place a check mark.
   Measurement for the selected group appears.

5. Click on the button next to the measurement name displayed on the red line to place a check mark.
   The parameter setting range of the selected measurement appears.
   Since **Filename / Comment / Slot / Solvent / Temperature / Temp.State** in the displayed parameters is already set up in the **Automation** window, re-setting is not necessary.

6. Select a parameter to change from the parameter list.
   The selected parameter is highlighted, and the input box to the side displays the value of the present parameter.

7. Change the parameter value.
8. Repeat steps 6-7 if necessary.
9. After parameter change is complete, click on the **Run with Changes** button.
   Automatic measurement starts.
   If you click the **Run with Default** button, automatic measurement will start after returning measurement parameter to the default value.

How to change a parameter other than the parameters displayed

When changing parameters other than the parameters displayed in the list box, perform the following procedure:

1. Click on the **Initialize** button in the **Set Parameters** window.
   The **Choose Parameter** window opens.

Fig. 2.37 Choose Parameter window

2. Select the parameter to add from the **Choose Parameter** window.
3. Click on the **Add** button.
4. Repeat steps 2-3 if necessary.
5. Click on the **Done** button after selecting all the parameters to add.
   The **Choose Parameter** window is closed, and the contents of the parameter list are updated.
6. Select the added parameter from the parameter list in the **Set Parameters** windows.
   The selected parameter is highlighted, and the input box to the side displays the value of the present parameter.

7. Change the value of a parameter.
8. Repeat steps 6-7 if necessary.
9. After parameter change is complete, click on the **Run with Changes** button.
   Automatic measurement starts.

2.5 RUN SAWTOOTH EXPERIMENT WINDOW

If you click on the **Sawtooth** button in the **Spectrometer Control** window, the **Run Sawtooth Experiment** window that displays a swept lock signal opens.

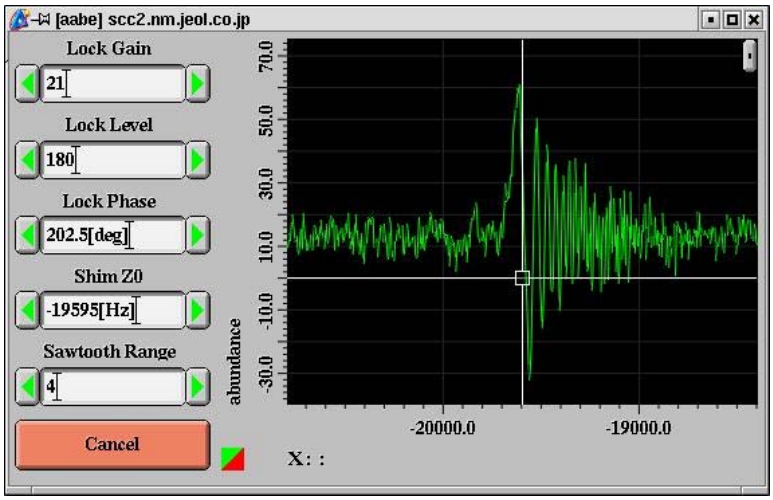


Fig. 2.38 Run Sawtooth Experiment window

This function is used when verifying a lock signal. When automatic locking does not function or composition of the deuterated solvent in a sample differs from the normal (example:10%D20, mixed solvent, and other), this function is used to verify a lock signal. When exchanging a sample, it is not needed.

Sawtooth display like other measurement performs one signal measurement. Therefore, the Queue is displayed on the **Spectrometer Control** window. Sometime is required until the first data is acquired after reading a pulse sequence. Moreover, data is not displayed on the **Run Sawtooth Experiment** window until the first acquisition is terminated.

The name **Sawtooth** arises from the waveform of the sweep of the Z0 magnetic field. The Z0 shim coil sweeps the magnetic field range specified with a **Sawtooth Range**. A **s**awtooth signal (a signal in the sweep width of sawtooth) will be observed if a lock signal lies in this range.

When you cannot observe a lock signal, set the Lock Level to 255 maximum first. When you still cannot find a signal, set the Sawtooth Range to 8 for the greatest range. If a lock signal is found, set the mouse pointer to **Pick Position** in the **Pick** mode using the cursor tool, and click on the lock signal. Z0 is automatically corrected so that the lock signal may come to the center of the screen.

C I

2.6 VECTOR VIEWER WINDOW

If you click on the **View** button in the **Spectrometer Control** window, the **Vector View** window that displays the spectrum during measurement opens.

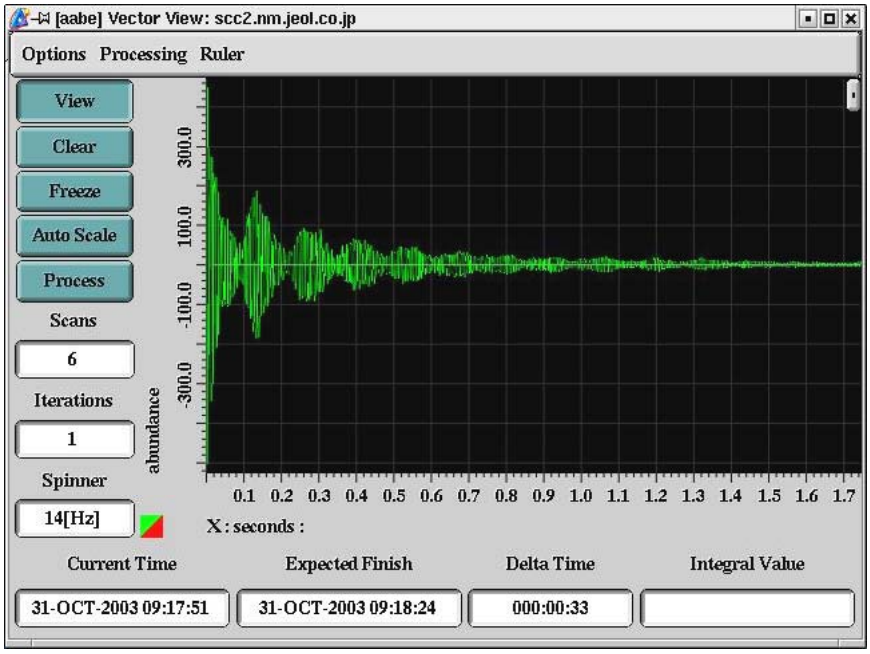


Fig. 2.39 Vector View window

The **Vector View** window has the function which displays a spectrum on real time as the data monitor during measurement.
If you click on the **View** button in the **Vector View** window, the present data is transmitted from the spectrometer to the screen. In addition, a transmission interval is an interval specified by **mod return** in the **Acquisition** section of the **Experiment** window. For example, if the value of **mod return** is set to 2, data is transmitted for every two accumulations. A load for a network increases when you shorten the updating interval of the data. So try to set a suitable value.

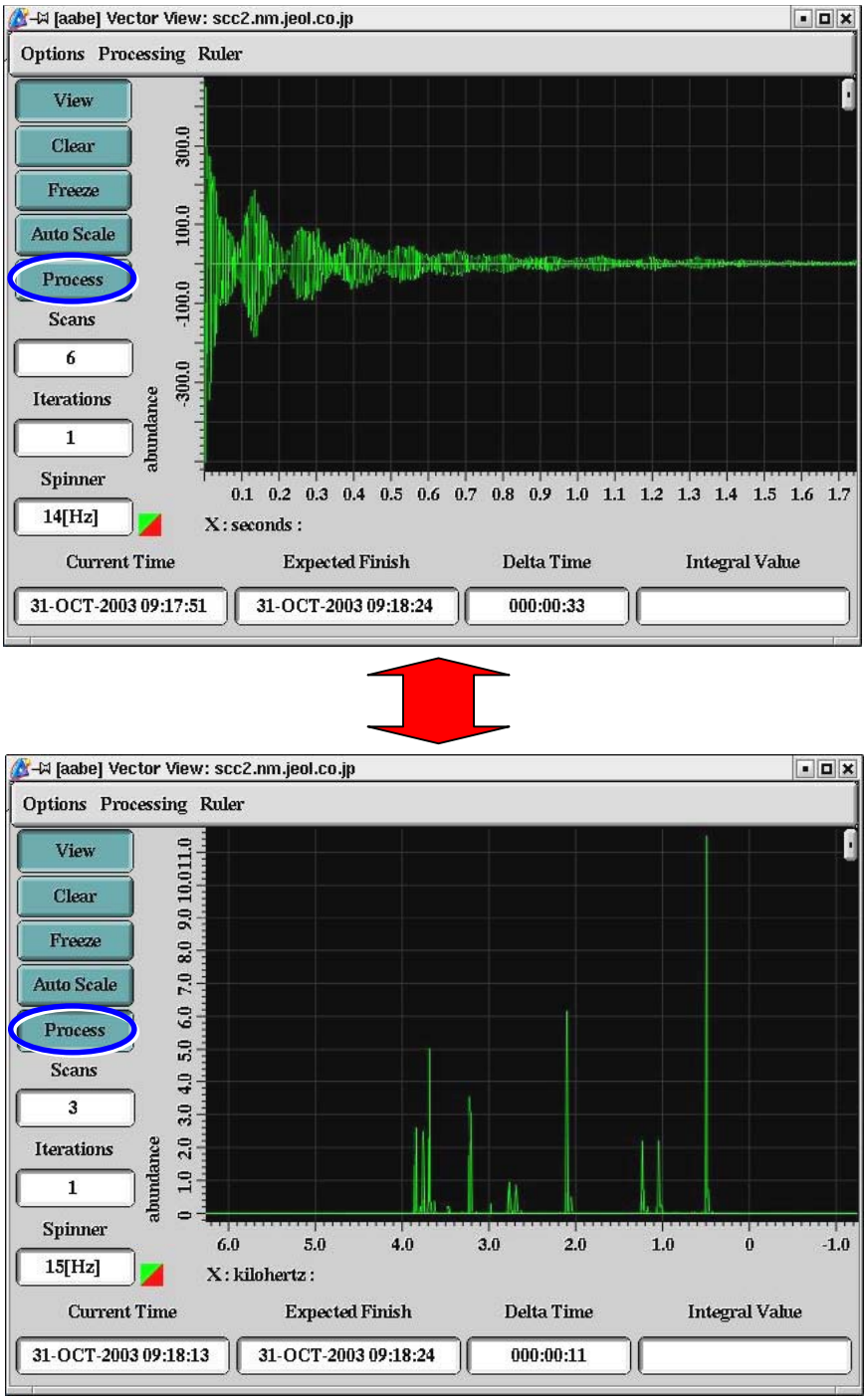
✍ Updating time for a spectrum in the **Vector View** window lasts until an accumulation is terminated from the state where the **View** button was clicked. If the updating time of a spectrum exceed 5 minutes, the **View** button turns OFF automatically. This is for reduces the load to a network. Once again, if you click on the **View** button, an updating spectrum is restarted.

✍ Even if the parameter specified to the **mod return** parameter is 1, when data points are too many or **Acquisition time** and **relaxation delay** are extremely short, or when the load of a network is large, an updating spectrum cannot be performed at the interval specified.

2.6.1 Changing a Display

This is the method of changing a FID display and a processed data display in the **Vector View** window.

1. Click on the **Process** button in the **Vector View** window.
   It changes to the processed data display.
2. Click on the **Process** button again.
   It returns to the FID display.



C I

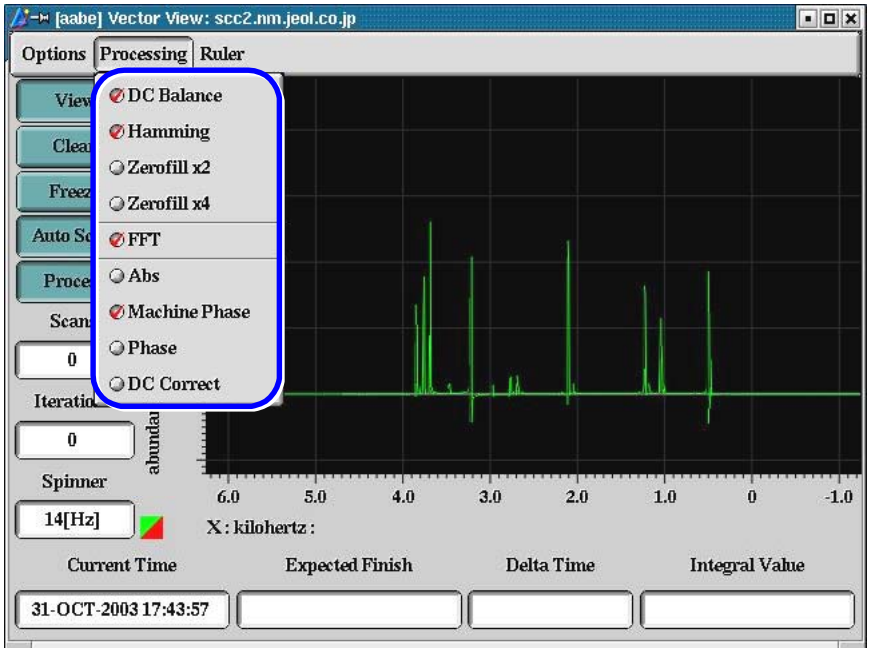
2.6.2 Processing Menu

The contents of processing can be selected in the **Vector View** window during processed data display.

◆ Select the menu displayed in **Processing** of the menu bar in the **Vector View** window.

Processing of the function by which the check mark is placed is them performed.

Function	Explanation
DC Balance	Corrects the DC component of FID.
Hamming	Multiplies Hamming window.
Zero fill x2	Performs 2 times zero filling
Zero fill x4	Performs 4 times zero filling
FFT	Performs FFT.
Abs	Performs an absolute value display.
Machine Phase	Performs automatic phase correction.
Phase	Performs phase correction.
DC Correct	Performs baseline correction.



C I

2.7 MAKE A NEW INSTANCE OF A SELECTED JOB COMMAND

You can copy the data in the middle of a **measurement**, and process it data using **1D Processor** and **nD Processor**. This function is used when verifying the progress in the middle of an accumulation.

- Click on the **Copy** button in the **Spectrometer Control** window.
  The data in the middle of measurement is copied, and **1D Processor** or **nD Processor** starts.

C I

2.8 90° PULSE WIDTH DISPLAY

90° pulse width for each measurement nucleus and the attenuator value which are described in a probe file can be displayed.

◆ Select **Tools–90's** in the menu bar of the **Spectrometer Control** window.
90° pulse width display window opens.

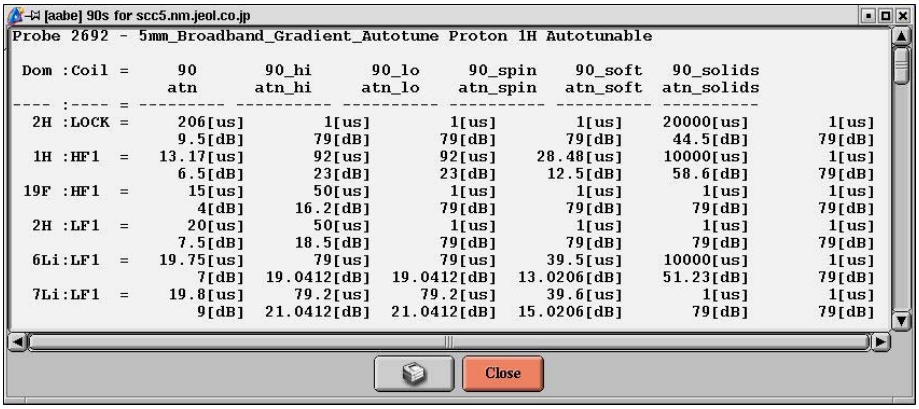

[aabe] 90s for scc5.nm.jeol.co.jp
Probe 2692 - 5mm_Broadband_Gradient_Autotune Proton 1H Autotunable
Dom :Coil = 90 90_hi 90_lo 90_spin 90_soft 90_solids
atn atn_hi atn_lo atn_spin atn_soft atn_solids
2H :LOCK = 206[us] 1[us] 1[us] 1[us] 20000[us] 1[us]
9.5[dB] 79[dB] 79[dB] 79[dB] 44.5[dB] 79[dB]
1H :HF1 = 13.17[us] 92[us] 92[us] 28.48[us] 10000[us] 1[us]
6.5[dB] 23[dB] 23[dB] 12.5[dB] 58.6[dB] 79[dB]
19F :HF1 = 15[us] 50[us] 1[us] 1[us] 1[us] 1[us]
4[dB] 16.2[dB] 79[dB] 79[dB] 79[dB] 79[dB]
2H :LF1 = 20[us] 50[us] 1[us] 1[us] 1[us] 1[us]
7.5[dB] 18.5[dB] 79[dB] 79[dB] 79[dB] 79[dB]
6Li:LF1 = 19.75[us] 79[us] 79[us] 39.5[us] 10000[us] 1[us]
7[dB] 19.0412[dB] 19.0412[dB] 13.0206[dB] 51.23[dB] 79[dB]
7Li:LF1 = 19.8[us] 79.2[us] 79.2[us] 39.6[us] 1[us] 1[us]
9[dB] 21.0412[dB] 21.0412[dB] 15.0206[dB] 79[dB] 79[dB]
Close

Fig. 2.40 90° pulse width display window

✍ This window can only display the contents of a probe file, and cannot change the value in the probe file.

C I

2.9 DISPLAYING AND CHANGE OF AN INSTRUMENT PARAMETER

Display and change of an instrument parameter can be performed.

2.9.1 Display of an Instrument Parameter

1. Select **Tools–Params** in the menu bar of the **Spectrometer Control** window.
   The **Params** window opens.

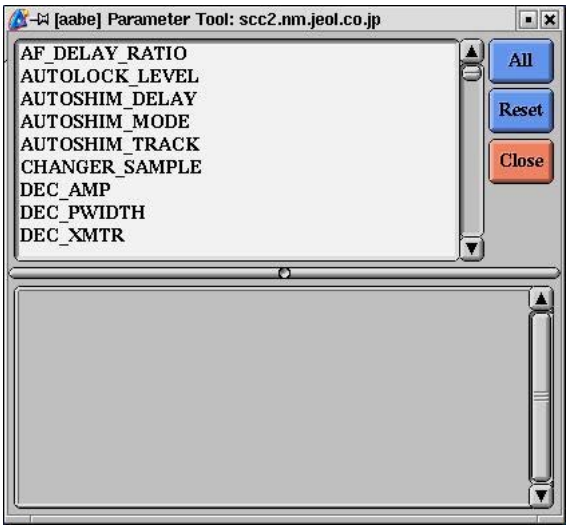


Fig. 2.41 Params window

2. Select a parameter to display parameter value with a mouse.
   The selected parameter is highlighted, and the value of a parameter is displayed.

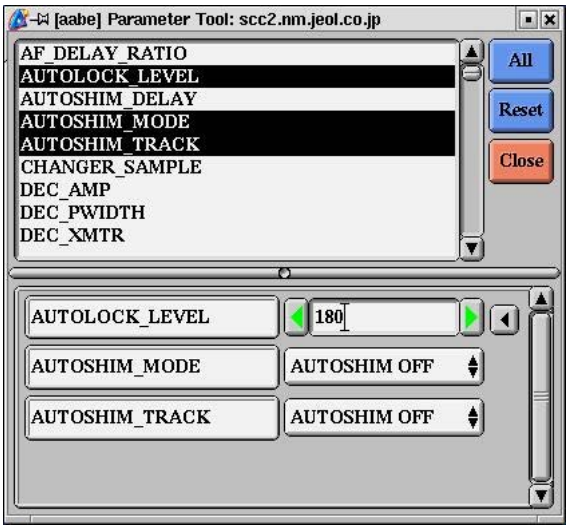


Fig. 2.42 Display of the parameter

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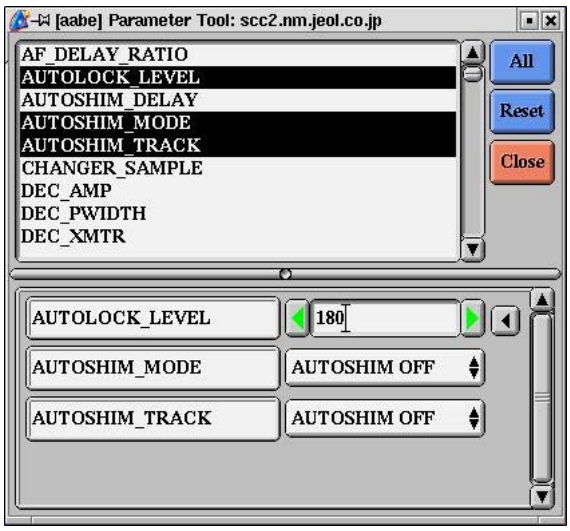
2.9.2 Changing an Instrument Parameter

1. Select the parameter to change, and display the parameter value.



2. Input the parameter value into the parameter input box into the right of the parameter name.

- The only parameter that can be changed is the parameter displayed on the parameter display box.
- Parameter related directly to execution of a pulse sequence, such as pulse width and pulse waiting time can be changed only in a part.

If the value of a parameter is changed in this window, since value is immediately sent to a spectrometer and the state of a spectrometer will its change, cautions are required even if the spectrometer is under measurement.

2.10 SHAPE VIEWER

A tool which a Shaped pulse or a noise source can be viewed is provided by Delta. Three kinds of **FG Shape**, **RF Shape**, and **Noise** can be displayed.

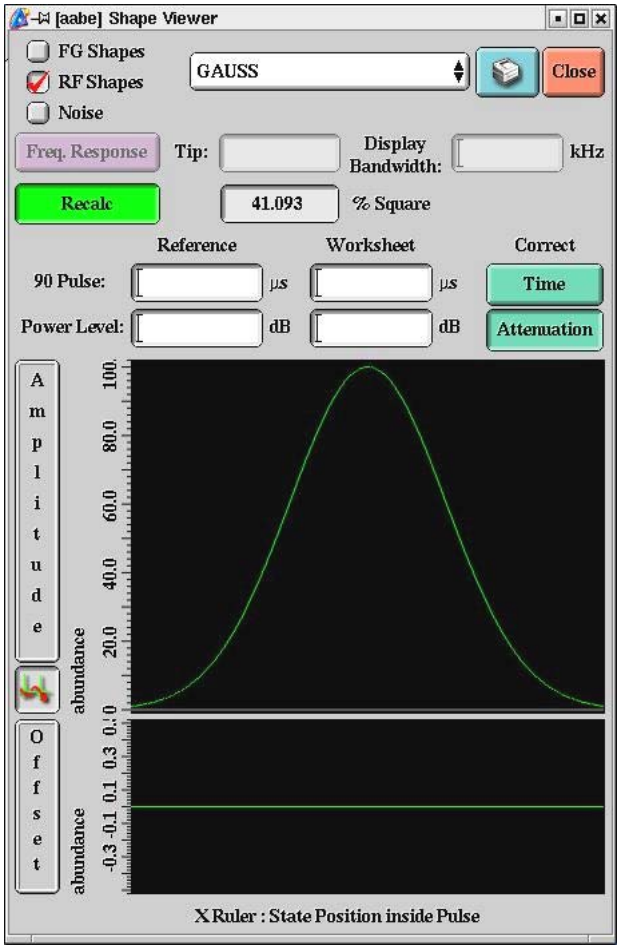


Fig. 2.43 Shape Viewer window

C I

2.10.1 How to Display a Shape

1. Select **Tools–Shape Viewer** in the menu bar of the **Spectrometer Control** window.
   The **Shape Viewer** window opens.
2. Select the category to display from **FG Shapes**, **RF Shapes**, and **Noise**.
3. Select a Shape to display.
4. Change **Phase** and **Amplitude** with the toggle button.

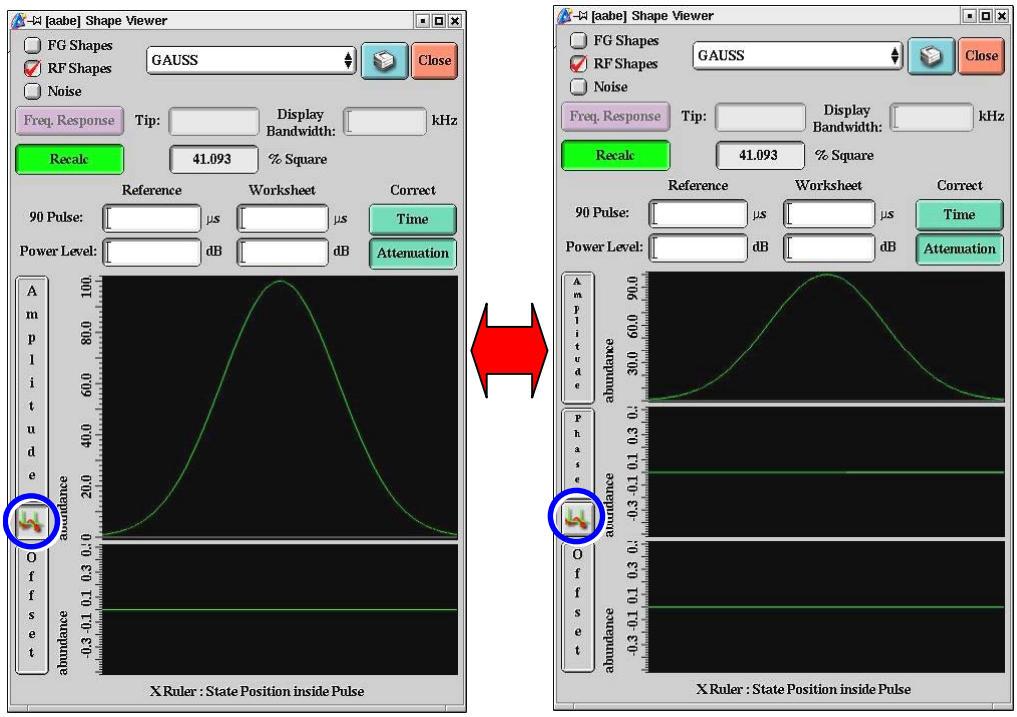
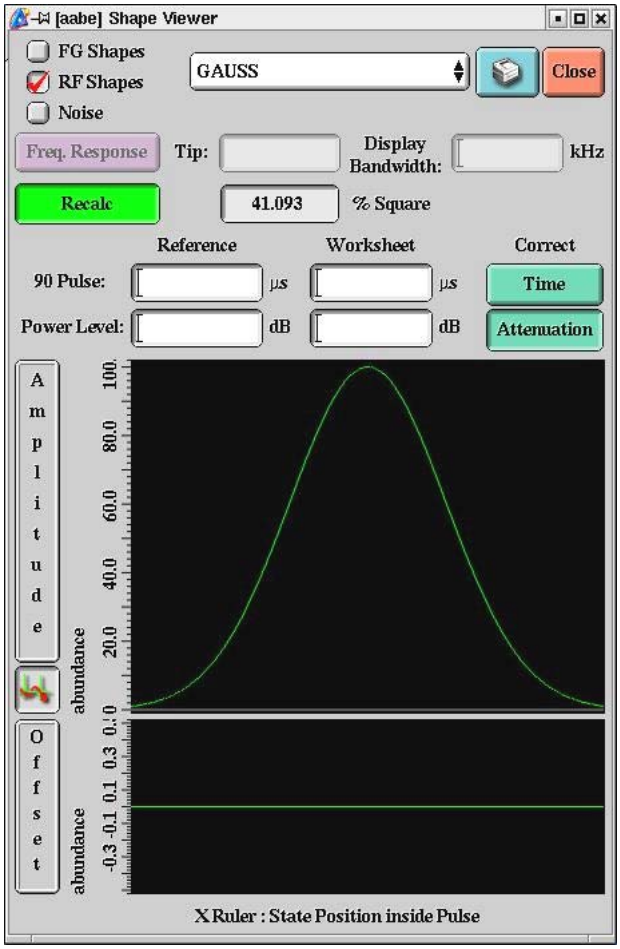


Fig. 2.44 Change Phase and Amplitude using the toggle button

2.10.2 Calculation of Pulse Width and Attenuator Value

Calculate and display the pulse width and the attenuator value of a shaped pulse in the **Shape Viewer** window.

Only **RF Shapes** provides a target for calculation.



1. Enter a value into **Reference** of **90 Pulse** and **Power Level**.
2. Enter a value into **Worksheet** of **90 Pulse** or **Power Level**.
   The remaining value is calculated from the entered value and the **Reference** value.

C I

2.11 ABNORMAL DISPLAY OF A SPECTROMETER

◆ Select **Tools**–**Status** in the menu bar of the **Spectrometer Control** window.

The situation of the alarm of a spectrometer is investigated, and the result is displayed on **Delta Console**.

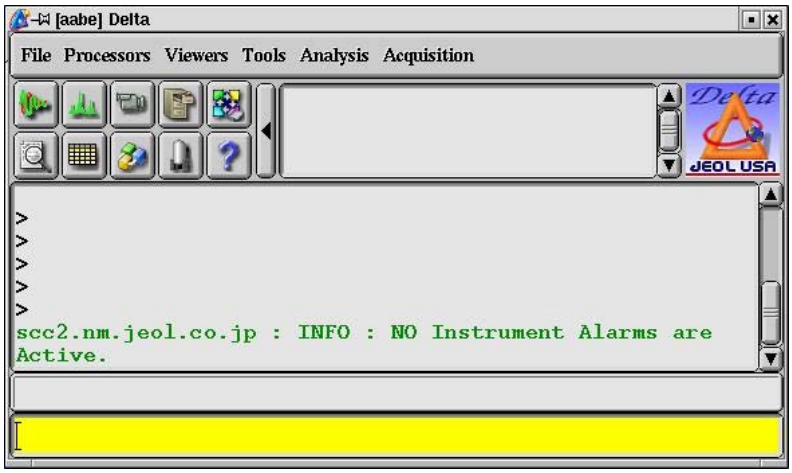

[aabe] Delta
File Processors Viewers Tools Analysis Acquisition
JEOL USA
scc2.nm.jeol.co.jp : INFO : NO Instrument Alarms are Active.

Fig. 2.45 Display of the spectrometer alarm on Delta Console

✍ A transitional error may be reported if this check button is carried out immediately after starting the system. Perform recheck after carrying out loading of a sample, NMR lock, and measurement.

2.12 VALIDATION

This verifies whether software is correctly installed in the spectrometer control computer.

2.12.1 Executing Validation

1. Select **Tools–Validation** in the menu bar of the **Spectrometer Control** window.

   The **Delta Installation Validation** window opens.

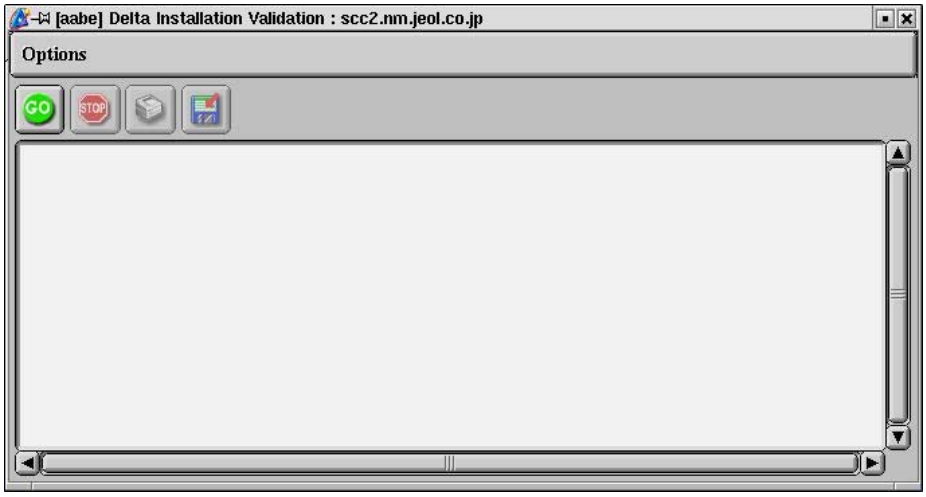


Fig. 2.46 Delta Installation Validation window

2. Click on the **Go** button.

   The check of a file is performed and the result is displayed.

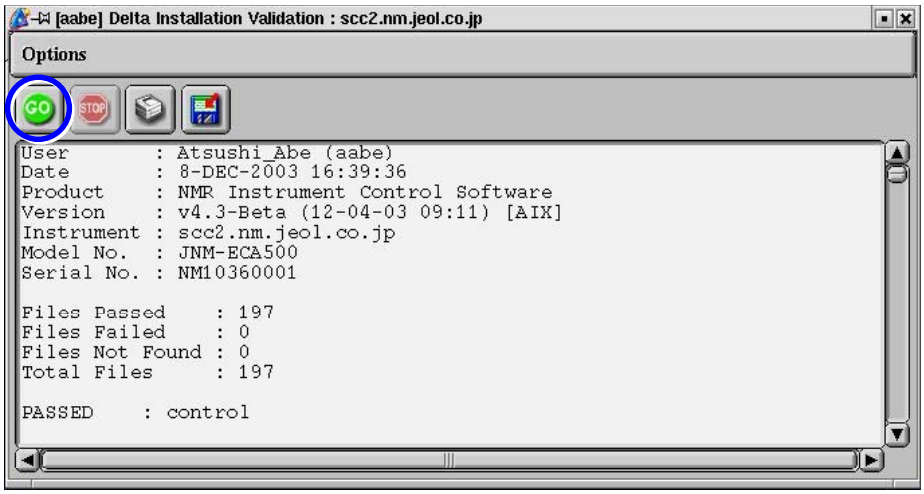


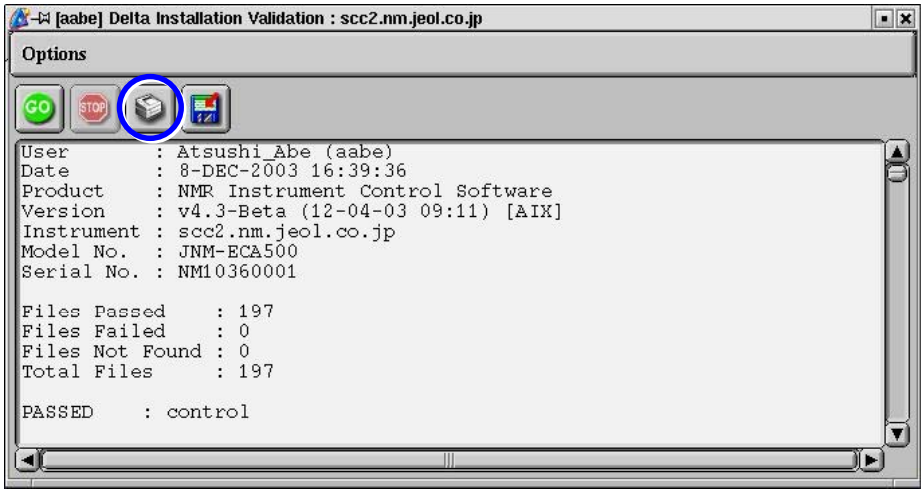
Fig. 2.47 Display of Validation result

C I

2.12.2 Printing Validation Result

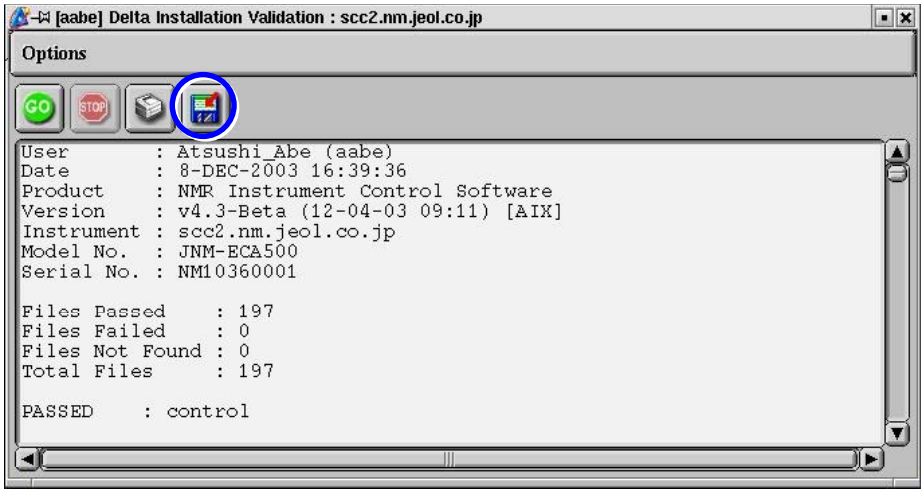
◆ Click on the **Print the results** button in the **Delta Installation Validation** window.

The **Validation** result is printed to the default printer.



2.12.3 Saving Validation Results to a File

1. Click on the **Save the results** button in the **Delta Installation Validation** window.



The **Save file** window opens.

2. Input a saving file name into the **Name** input box after moving to the directory to save, and click on the **Ok** button.

The **Validation** result is saved.

When creating a new saving directory, click on the button after specifying a directory name to the **Path** input box. Create and transfer the directory. Then, the saving file name is entered into the file name input box.

C I

2.13 DISPLAY OF LOG FILE

This displays the spectrometer log.
Three kinds of **Cryogen Log, Machine Log**, and **Queue Log** are saved as a log.

2.13.1 Cryogen Log

◆ Select **Tools–View Log File–View Cryogen Log** in the menu bar of the **Spectrometer Control** window.
The **Cryogen Log** window opens.

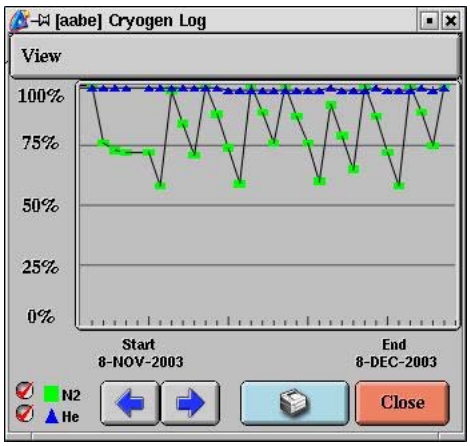


Fig. 2.48 Cryogen Log window

✍ A display can be selected from Month, Quarter, and Year. The display can be changed by selecting **Month**, **Quarter** or **Year** selecting **View** from the menu bar in the **Cryogen Log** window.

✍ The front screen or the following screen can be displayed by clicking on the arrow button.

■ Plotting log

Click on the Plot Cryogen Graph button in the Cryogen Log window to plot the graph.

C I

2.13.2 Machine Log

- Select **Tools–View Log File–View Current Machine Log** in the menu bar of the **Spectrometer Control** window.
  The **View machine.log** window opens.

[aabe] View machine.log
5-DEC-2003 10:14:45 INFO : Connection established by aabe(atsushi_a
5-DEC-2003 10:15:40 L : INFO : Changer Selecting Sample 1
5-DEC-2003 10:15:40 L : INFO : Changer Retrieving Sample
5-DEC-2003 10:15:40 L : INFO : Changer Loading Sample
5-DEC-2003 10:15:52 L : INFO : Changer Loaded Sample
5-DEC-2003 10:16:18 INFO : Disconnection by aabe(atsushi_abe)
5-DEC-2003 10:23:58 INFO : Connection established by aabe(atsushi_a
Close

Fig. 2.49 View machine.log window

■ Display of an old Machine.log

- Select **Tools–View Log File–View Old Machine Log** in the menu bar of the **Spectrometer Control** window.
  The **View machine.log.old** window opens.

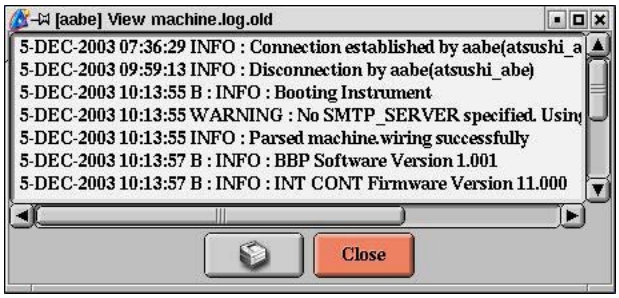

[aabe] View machine.log.old
5-DEC-2003 07:36:29 INFO : Connection established by aabe(atsushi_a
5-DEC-2003 09:59:13 INFO : Disconnection by aabe(atsushi_abe)
5-DEC-2003 10:13:55 B : INFO : Booting Instrument
5-DEC-2003 10:13:55 WARNING : No SMTP_SERVER specified. Usin
5-DEC-2003 10:13:55 INFO : Parsed machine.wiring successfully
5-DEC-2003 10:13:57 B : INFO : BBP Software Version 1.001
5-DEC-2003 10:13:57 B : INFO : INT CONT Firmware Version 11.000
Close

Fig. 2.50 View machine.log.old window

■ Plotting log

A log can be printed by clicking on the **Print** button in the **View machine.log** window, or the **View machine.log.old** window.

2.13.3 Queue Log

- Select **Tools–View Log File–View Current Queue Log** in the menu bar of the **Spectrometer Control** window.
  The **View queue.log** window opens.

[aabe] View queue.log
5-DEC-2003 10:28:46 00_001 aabe(atsushi_abe) as Atsushi_Abe Deuter
5-DEC-2003 10:29:45 00_002 aabe(atsushi_abe) as Atsushi_Abe Deuter
5-DEC-2003 16:57:11 00_004 kurimoto(delta) as delta nbn ccc single_pu
5-DEC-2003 17:00:43 00_005 kurimoto(delta) as delta nbn ccc single_pu
8-DEC-2003 08:49:56 00_006 kurimoto(delta) as delta nbn ccc single_pu
8-DEC-2003 08:50:58 00_007 kurimoto(delta) as delta nbn ccc single_pu
8-DEC-2003 08:51:08 00_008 kurimoto(delta) as delta nbn ccc single_pu
Close

Fig. 2.51 View queue.log window

■ Display of old Queue.log

- Select **Tools–View Log File–View Old Queue Log** in the menu bar of the **Spectrometer Control** window.
  The **View queue.log.old** window opens.

Fig. 2.52 View queue.log.old window

■ Plotting log,

A log can be printed by clicking on the **Print** button of the **View queue.log** window or the **View queue.log.log** window.

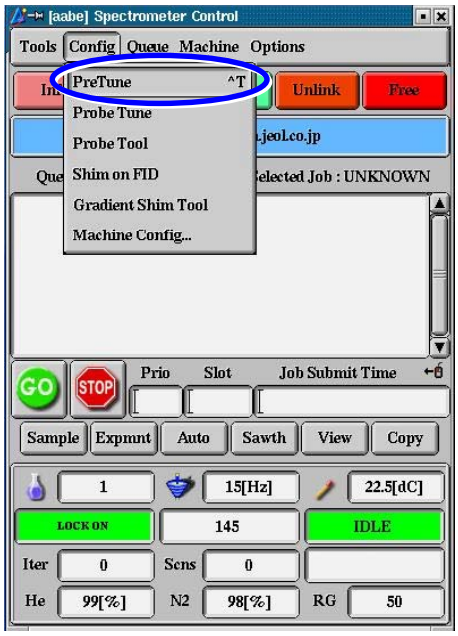
C I

2.14 PRE TUNE

When using an autotuning unit, it is necessary to set up the dial value of the probe in advance. **Pre Tune** performs these settings.
Pre Tuning is performed by the following procedure.

1. Select **Tools–Mode-Console** in the menu bar of the **Spectrometer Control** window.

2. Select **Config–PreTune** in the menu bar of the **Spectrometer Control** window.



The Config Autotune Probe window opens.

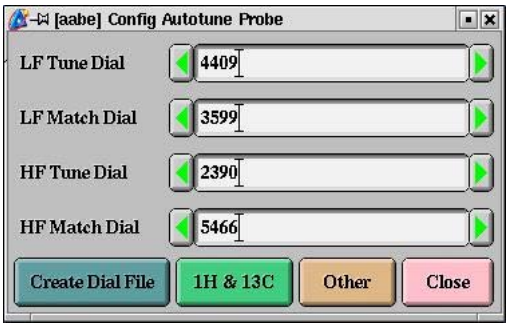
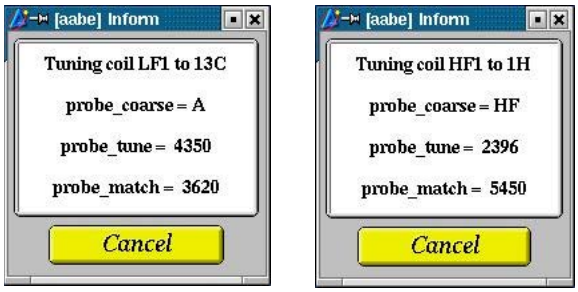


Fig. 2.53 Config Autotune Probe window

3. Read the dial value of the auto-tuning probe, and enter a dial value into each input box.

4. Click on the **1H &13C** button.
   The check window of a dial value appears.

5. Click on the **OK** button after confirming that the dial value is set correctly.
   Dial value is saved and **Pre Tuning** begins.
   Pre Tuning is performed in the order of Coarse, LF, and HF. The following dialog boxes are displayed during the **Pre Tuning** of LF and HF.



6. After the dialog box of HF disappears and **Pre Tuning** is complete, click on the **Close** button in the **Config Autotune Probe** window to close the window.

7. Click on the **Connect** button in the **Spectrometer Control** window to return the connection mode to Connect mode.

C I

2.15 PROBE TUNE

This performs tuning on the specified nucleus. Although tuning can also be performed at measurement, when tuning before measurement, tuning is performed by the following procedure.

1. Select **Config–Probe Tune** in the menu bar of the **Spectrometer Control** window.
   The **Probe Tune Tool** window opens.

Fig. 2.54 Probe Tune Tool] window

2. Select the coil to tune in **Coil**.
3. Select the nucleus to tune in **Domain**.
4. Set an **Offset** if necessary.
5. Click on **Force Tune**.
   Unless a check mark is placed in **Force Tune**, the tuning of a nucleus which has already been tuned is not performed.
6. Click on the **Tune Now** button.
   Tuning starts.
7. Click on the **Close** button after tuning is complete.
   The **Probe Tune Tool** window closes.

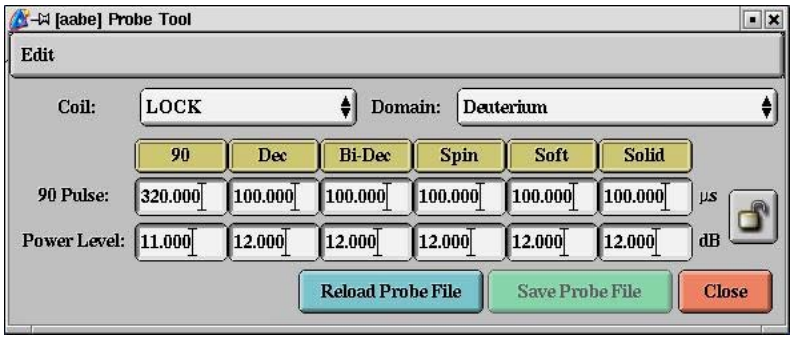
C I

2.16 PROBE TOOL

This displays information on the specified nucleus in the probe file. Moreover, in Console mode, a probe file can be rewritten.

2.16.1 Display of Information for a Specified Nucleus

1. Select **Config**–**Probe Tool** in the menu bar of the **Spectrometer Control** window.
   The **Probe Tool** window opens.



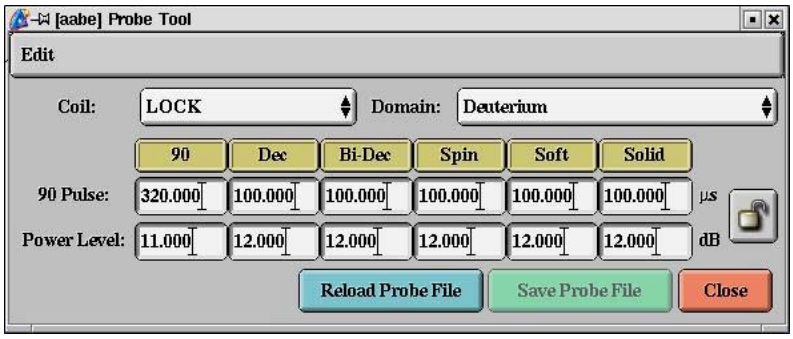
2. Select a coil in **Coil**.
3. Select a nucleus in **Domain**.
   A 90° pulse width for the specified nucleus and information on attenuator value are displayed.

C I

2.16.2 Saving a Value to the Probe File

1. Select **Tools**–**Mode**–**Console** in the menu bar of the **Spectrometer Control** window.

2. Select **Config**–**Probe Tool** in the menu bar of the **Spectrometer Control** window.
   The **Probe Tool** window opens.



3. Select a coil in **Coil**.
4. Select a nucleus in **Domain**.
   The 90° pulse width of the specified nucleus and information on attenuator value are displayed.
5. Correct value.
6. Click on the **Save Probe File** button.
   The probe file is updated.

C I

2.17 SHIM ON FID

You can adjust the resolution in one window while viewing an actual spectrum. You can adjust the resolution while actually verifying situations of the signal, such as the shape of the skirt portion of a peak, and the line width of a peak as measured.

1. Select **Config**–**Shim on FID** in the menu bar of the **Spectrometer Control** window.

The **Shim ON FID** window opens.

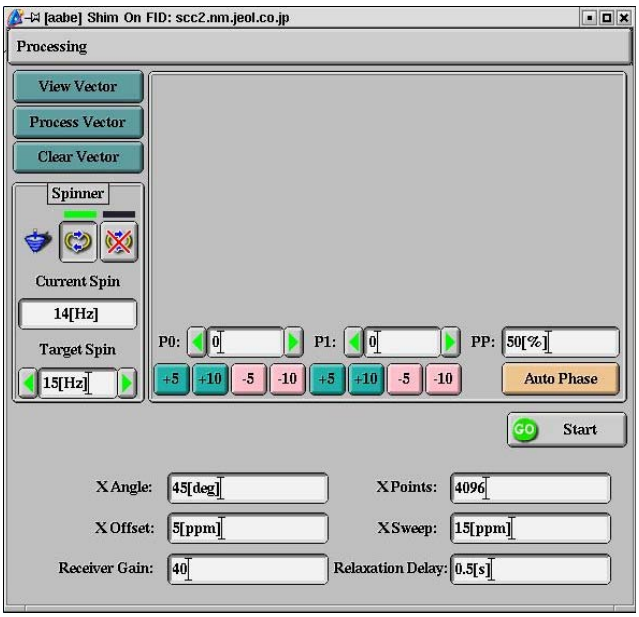
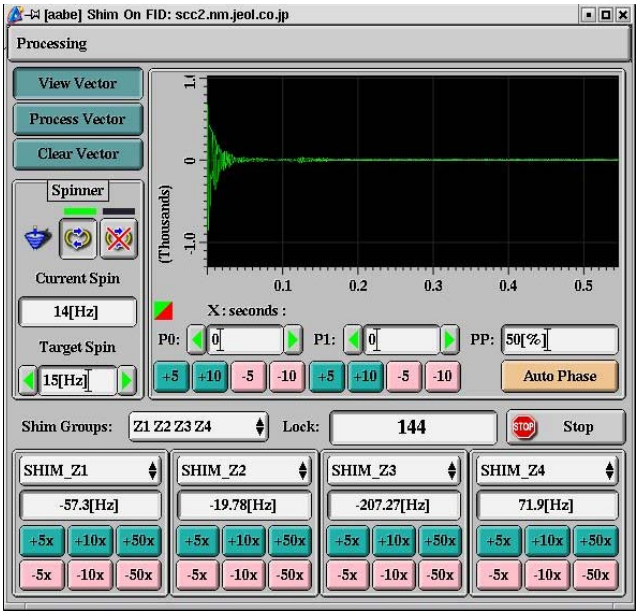


Fig. 2.55 Shim ON FID window

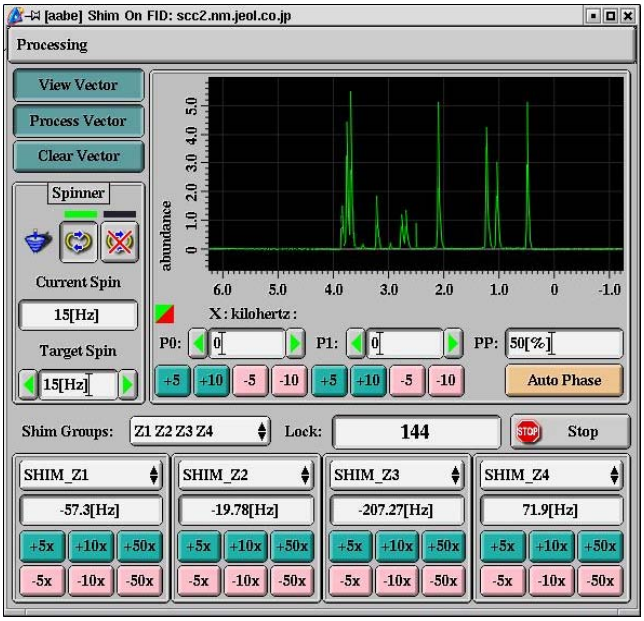
2. Click on the **Start** button.

A spectrum is displayed.



C I

3. In order to display processed data, click on the **Process Vector** button.



For the contents of processing, place a check mark next to the processing item in **Processing** the menu bar.

4. Click on the **Go** button.
Data acquisition begins. Data is continuously updated.

5. Selecting the shim axis to display by **Shim Group**.

6. Adjust the resolution while viewing a spectrum.

7. Click on the **Stop** button after resolution adjustment is complete.
Updating the data stops.

8. Close the **Shim ON FID** window.

2.18 GRADIENT SHIM TOOL

2.18.1 Outline of the Gradient Shim

The resolution adjustment (shim adjustment) is carried out to adjust the current running through the multiple shim coils inside the SCM so that the magnetic field applied to the sample becomes uniform. Each shim coil produces a magnetic field of a different shape. These fields are added to correct the inhomogeneous magnetic field.

The basic correction magnetic fields are the axial shim terms Z1 to Z6 used to correct the axial magnetic field of the sample and the radial shim terms such as X1, Y1, and XZ used to correct the horizontal magnetic field. The actual correction magnetic field is a composition of shim terms multiplied by the coefficients. In other words, the shim adjustment is carried out to adjust the coefficient applied to these shim terms.

■ Feature of the gradient shim

Conventional shim adjustment searches for the combination of shim values that maximizes the signal intensity while monitoring the lock signal intensity. Generally, the automatic adjustment function called simplex is used. This method requires more time as the number of types of shims used increases. Manual shim adjustment requires some experience. If the initial shim condition is bad, it takes considerable time for even a skilled operator to adjust the shims. Using the gradient shim, anyone can easily increase the resolution, even if the number of the shims increases. You can adjust the shims from Z1 to Z6 in a few minutes, regardless of the initial shim conditions.

When the gradient shim is used, the magnetic field distribution (the magnetic field map) over the sample is measured using the magnetic field gradient.
The combination of the coefficients of the basic map that makes the field map uniform is computed, and the shim system is set to it. Then, the magnetic field map is measured again. These measurements and computations are iterated until the field map becomes sufficiently uniform. The computer does these tasks, so in practice, the operation is simply to insert the sample and click on the button. A single line of ^{2}H or ^{1}H contained in the sample is used to measure the magnetic field map. The axial shim terms, Z1 to Z6, can be adjusted as the Field gradient of the Z1 axis is used.

✍ Calibration (creating the basic map)
When the gradient shim is used, the shim terms Z1 to Z6 are calculated based on the correction magnetic field.
The correction magnetic field measured using the standard sample is called the basic map, and the measurement of the basic map is called calibration. Calibration varies depending on the probe in use and the measurement nucleus. However, calibration should be performed once, and it is not necessary to do so every time when the actual sample is measured. The basic map of Z1 to Z6 is stored in the directory /usr/people/delta/delta/instrument and is used to correct the magnetic field of the measurement sample.

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Gradient shim

In the gradient shim used in the spectrometer, there are two methods for homogeneity spoiling (homospoil) and PFG (Pulsed Filled Gradient). In this spectrometer, the homogeneity spoiling gradient shim, whose observed nucleus is ^{2}H, is provided as a standard, and the conditions that can be used the standard gradient shim for every probe is set. Moreover, the function in which the gradient shim can be easily performed only by clicking on an icon is also provided. A gradient shim is recommended if it satisfies these two conditions:

- The ^{2}H nucleus of a deuterated solvent can be used as an observed nucleus.
- Homogeneity spoiling can be applied for all spectrometers and probes.

✍ Solvent

- A **Selective Gradient** is used for gradient shimming of the solvent containing two or more ^{2}H signals like methanol-d4 or pyridine-d5. In a **Selective Gradient**, calibration is required (☞ separate volume "ADMINISTRATOR'S MANUAL").
- In the case of a normal water sample, since sensitivity of the D_2O signal is insufficient for a lock, an observed nucleus uses ^{1}H. In a ^{1}H gradient shim, calibration is required (☞separate volume "ADMINISTRATOR'S MANUAL").

2.18.2 Gradient Shim Operation

In the gradient shim operation, a method using the **Gradient Shim** button of the **Sample** window or a method using the **Gradient Shim Tool** can be used. Usually, the **Gradient Shim** button of the **Sample** window is used.
Each feature is shown below.

● The Gradient Shim button

Gradient Shim button **Gradient Shim and Lock** button

Click on one of above buttons to perform gradient shimming.
The Gradient Shim and Lock button turns on the NMR lock after executing gradient shimming. Usually, sufficient resolution can be obtained by operating these buttons. Early shim conditions are read from the system shim file. The conditions of the gradient shimming are fixed.

☞ Refer to Subsection 2.2.7 "■NMR lock control button" for more information on the usage.

● Gradient Shim Tool

Gradient shimming is performed under specified conditions. Change of the resolution can be verified by display of a magnetic field map. This gradient shim tool is used when good resolution cannot be obtained by the function of the above button, and when performing gradient shimming other than on a standard.

■ Preparation

Preparation before beginning gradient shimming is as follows. First load a sample into the SCM.

1. Open the **Sample** window and turn ON a spinner.
2. Specify a lock solvent from the **Solvent** list box.
3. Turn OFF an NMR lock.

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Starting Gradient Shim Tool

◆ Select **Config–Gradient Shim** in the menu bar of the **Spectrometer Control** window.

The **Gradient Shim Tool** window opens:

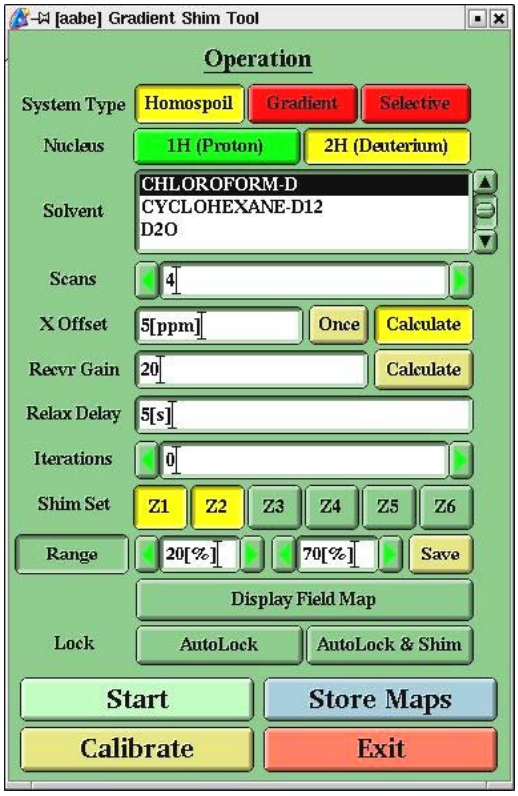

Fig. 2.56 Gradient Shim Tool window

Setting measurement conditions

1. Specify the type of the magnetic field gradient, and an observation nucleus.

System Type: **Homospoil** is turned ON.

Nucleus: **2H (Deuterium)** is turned ON.

2. Specify other measurement conditions.

Scans: Set the number of scans to accumulate (4 multiples).

X Offset: Click on the **Once** button, and turn on **Twice** and **Calculate.**
The resonance position of a signal is searched automatically by **Calculate**, and **X Offset** sets it to the observation center. **Once** corrects **X Offset** only once before performing gradient shimming. **Twice** adjusts it finely after the 1st iteration is terminated.

Recvr Gain: Turn on Calculate.
Receiver gain is adjusted automatically.

Relax Delay: Set the waiting time of the repetition pulse (5-8s).

Iterations: Set the number of times of iteration.
If it is 0, the number of times of iteration is judged automatically.

Shim Set: Turn on Z1, Z2, Z3, and Z4.
Specify the combination of the shim that performs gradient shimming.

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Range/%Width:

Usual measurement does not change. When [%Width] is 100% (when not specified), and When you use the sample whose liquid amounts are different such as micro cell, input the effective range which performs gradient shimming (☞refer to the subsequent page).

3. Turn ON **Display Field Map**.

Whenever 1 iteration is terminated, the magnetic field map is displayed. When **Display Field Map** is OFF, a map is not displayed.

4. Turn ON **AutoLock**.

Autolock is applied after you finish gradient shimming.

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Start and end of a gradient shim

1. Click on the **Start** button.

Gradient shimming starts and the job of gradient shimming is performed.
The **Gradient Shim Status** window opens, and the progress (in %) of the iteration is displayed.

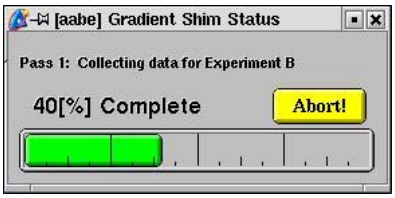

Fig. 2.57 Gradient Shim Status window

Whenever one iteration is terminated, the magnetic field map is displayed on the **Field Map** window. When several iterations are performed, they are all displayed.

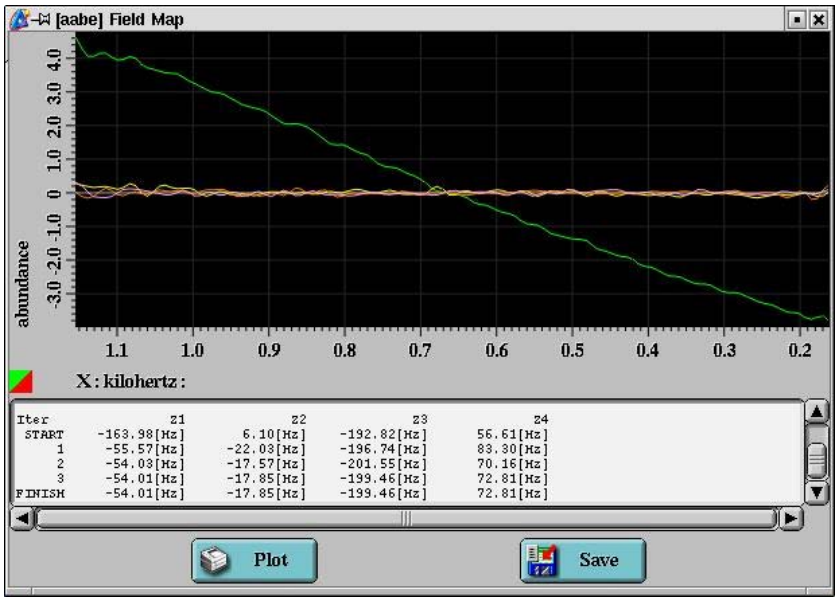

Fig. 2.58 Field Map window

2. Click on the **Exit** button after Gradient Shimming is complete.

The **Gradient Shim Tool** window closes.

Reference:

- When a good resolution is not obtained, increase the number of scans to accumulate. When the resolution is bad at the start, set many iterations (e.g., 3 instead of 0).
- Usually try to specify the shim settings for Z1, Z2, Z3, and Z4.
- Do not change parameter values during an operation. If they change, the measurement will be influenced.
- In the gradient shimming, a uniform sample is presupposed. If the homogeneity of a sample is bad, operation of the gradient shim will be affected. Especially when the solvent is water, take care to remove ant small bubble founded in a sample.

- In order to determine the effective range of the magnetic field map, set %Width to 1, set **Iterations** to 100%, and turn ON **Display Field Map**, then perform gradient shimming. The flat portion of the magnetic field map becomes the effective range. In order to make a percent display for the horizontal axis of the magnetic field map, select **Ruler–Percent** in the menu with the right mouse button.

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2.19 SPECTROMETER CONFIGURATION

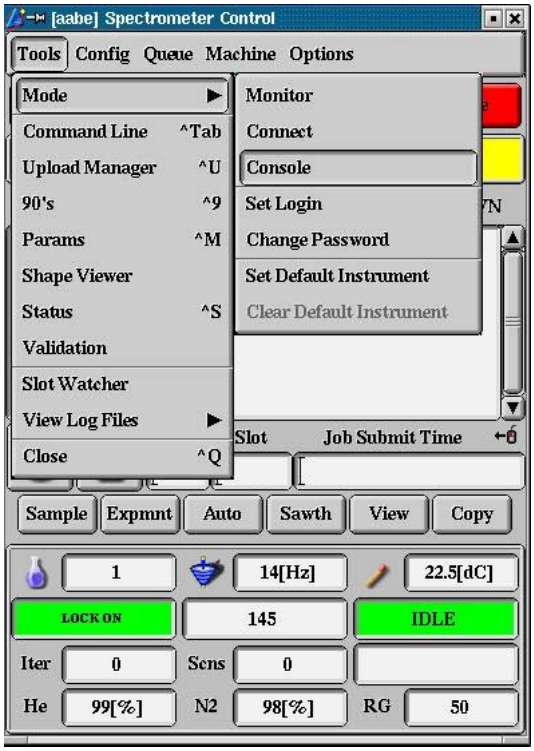
The tool which changes the spectrometer Configuration file is provided.

— CAUTION ————

Configuration files, such as machine.config file, are required for setting spectrometer information. When they are not correctly defined, not only an instrument does not operate correctly, but they also become the cause of instrument trouble.

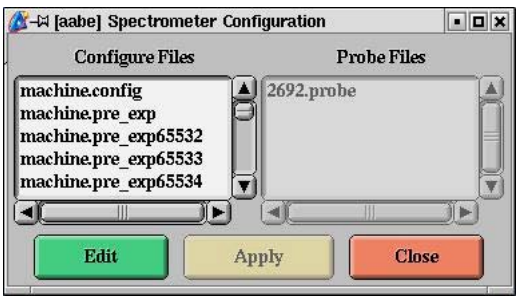
Since the configuration file is set up by commonly at the time of instrument delivery, do not usually change this file.

1. Select **Tools**–**Mode**–**Console** in the menu bar of the **Spectrometer Control** window.

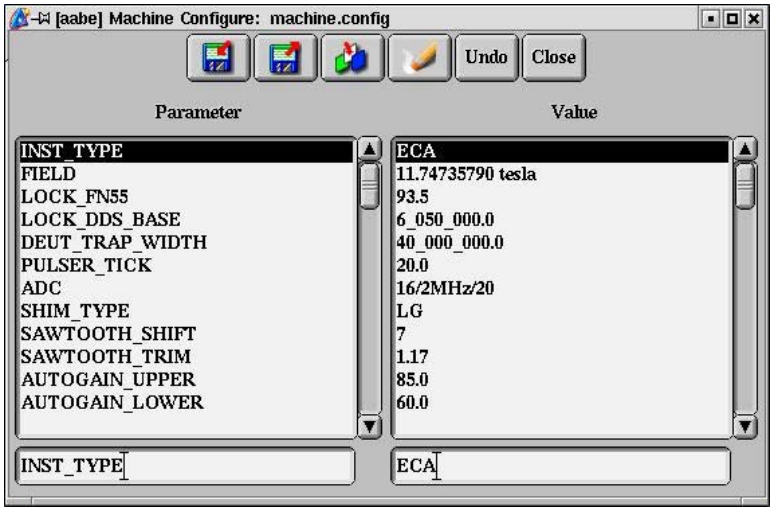


2. Select **Config**–**Machine Config..** in the menu bar of the **Spectrometer Control** window.

The **Spectrometer Configuration** window opens:



3. Select the file to edit from the **Configure Files** list box.
4. Click on the **Edit** button.
   The **Machine Configure** window opens.



5. Select the parameter to change from the **Parameter** list box.
6. Set a value in the **Value** input box.
7. Save a file to the **Save Configure File** (updating).

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2.20 EXPERIMENT AND QUEUE MANAGMENT

Queuing performs measurement in this spectrometer. That is, more than one experiment can be registered to the spectrometer (submit); and they are performed in the order of registration. There are five modes **OWNED**, **RUNNING**, **HALTED**, **FREE**, and **WAITING** in the spectrometer Queue. These modes cannot be changed if there is no console privilege.

A priority is given the measurement that is recorded in a Queue, respectively. The priority is ranked with numerical values from 0 (minimum) to 255 (maximum). Each user's default priority is specified as the "queue.priorities" file of the spectrometer management computer. A user can also change the priority of this measurement. However, possible change in ranking is only from higher to lower. If you have any console privilege, you can freely change the priority of all measurements.

2.20.1 Queue State

The present state of the Queue is displayed on the **Spectrometer Control** window.

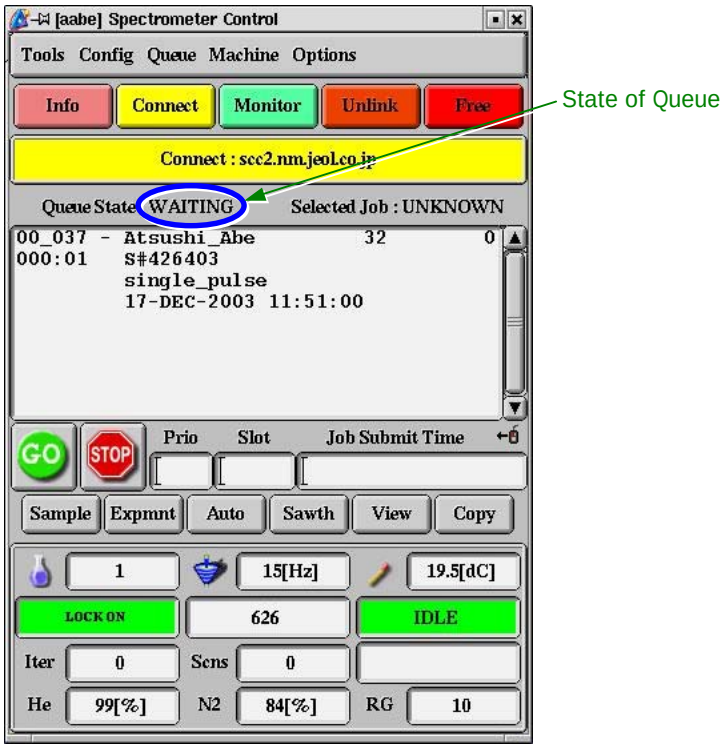

Fig. 2.59 State display of Queue

Hereafter, each state is explained:

State	Display	axplanation
Occupancy	**OWNED**	In the state where the system is connected with the spectrometer using the **Connect** button, a user can occupy a Queue (it is owned). Though other users record a measurement (experiment), only the user who connected previously using the **Connect** button can perform a measurement.
Measurment	**RUNNING**	In this state another user is performing measurement. Console privilege is required when changing the Queue.
Stop	**HALTED**	In this state, the Queue was stopped using the **Stop** command or **Hold** flag. If the Queue is restarted using the **Start** command, all measurements will restart.
Free	**FREE**	Queue is in a free state.
Waiting	**WAITING**	Measurement start time has been specified, and is in the state of waiting for an execution.

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2.20.2 Queue Menu

The command for controlling a Queue is provided in the **Queue** menu of the **Spectrometer Control** window.

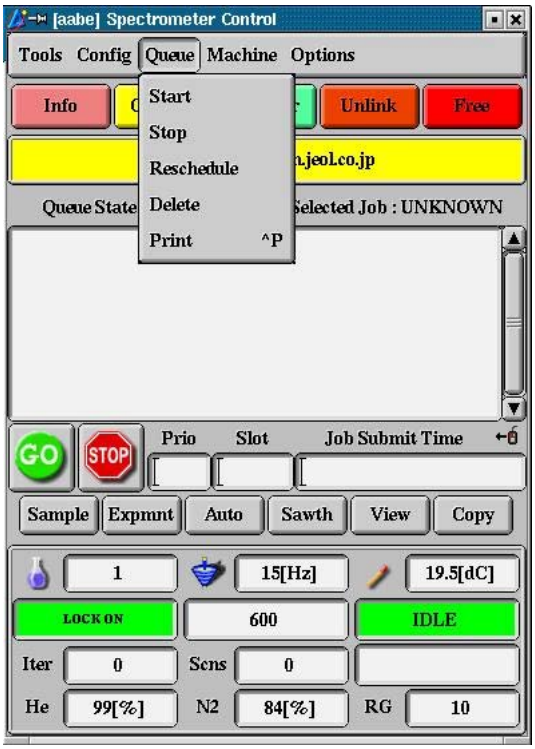

Fig. 2.60 Queue pull down menu

Menu	Detail
Start	Restarts a Queue stopped.
Stop	If you execute **the Stop** command after clicking to select a specified Queue, all subsequent Queues will be in a pause state. Since the function of the **Stop** command differs from the button, be careful.
Reschedule	The measurement that came to a head can be turned to the end of the Queue. It is used when a spectrometer is not ready with a certain reason.
Delete	The whole Queue is canceled except for the currently running measurement
Print	The recorded Queue is printed.

2.20.3 Restating Measurement (GO button)

Go button

Before performing the first experiment in the Queue, a spectrometer compares the name (sample_id) of the last measurement and measurement that it is going to perform from now. If the **sample_id** is the same, measurement is started immediately. When the **sample_id** is not on agreement or is not specified, measurement will be in the state of waiting for execution, and a message window will be displayed on a screen.
Here, the states of a sample (spinning of a sample tube and states of a shim) can be verified. If you click on the **GO** button, a pause state is canceled and measurement restarts.

Fig. 2.61 Check message window

Measurement that changes into waiting state for an execution with the Queue is as follows. Observe "**–**" displayed on the top line.

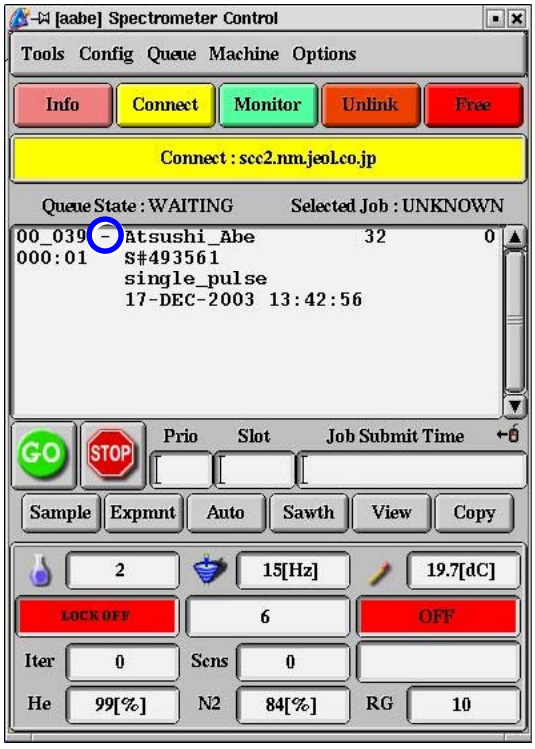

Fig. 2.62 Measurement (Spectrometer Control window) for an execution waiting state

If you click on the **GO** button, the following appears. Observe that "–" changes to "✱ ".

Fig. 2.63 Restarting measurement (Spectrometer Control window)

2.20.4 Cancelling Measurement (STOP button)

STOP button

The experiment that recorded in a Queue can be canceled using the following procedure.

1. Select the measurement to cancel.

Fig. 2.64 Selection of a measurement (Spectrometer Control window)

2. Click on the **STOP** button.

Several seconds are required before measurement is canceled by the state of a network and measurement repetition time. When **save aborted** of the **Experiment** flag was **True**, data is read while having been canceled and it is displayed on the **1D Processor** window. Data is deleted when it is not **True**. This flag is **True** unless the setting is changed.

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2.20.5 Measurement Priority

As described above, priorities from 0 to 255 exist in a measurement (experiment), and a measurement priority already recorded in a Queue can be changed in the **Spectrometer Control** window. If you select measurement and input a numerical value in the **Priority** input box, the order of measurement will change according to the priority. However, change of a common user's priority is only the change to the lower one. Measurement priority can be changed freely by a privilege user.

✍ Change to Queue under measurement cannot be performed now.

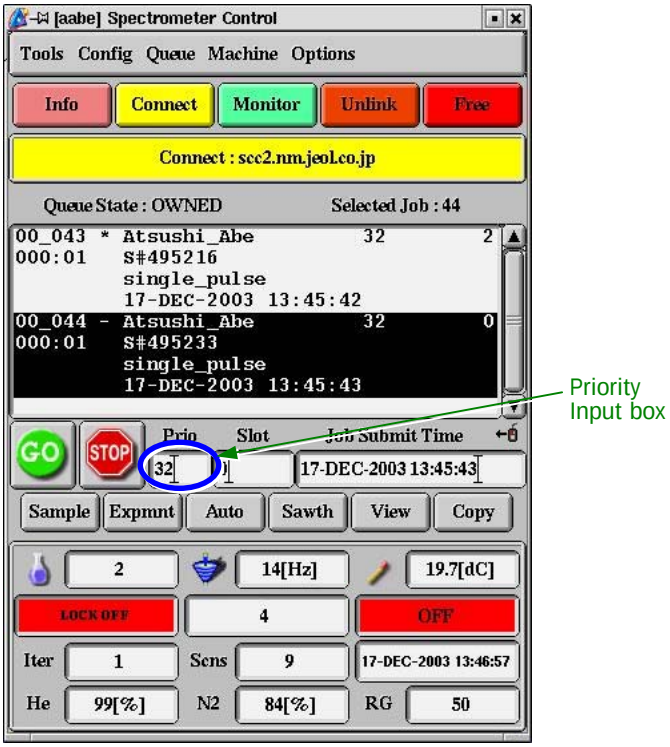

Fig. 2.65 Priority input

2.20.6 Slot

The **Slot** input box is specified when using an auto sample changer.

2.20.7 Start Time of Measurement

Although measurement is usually added to a Queue after recording an experiment, the start time of the added measurement can be delayed. However, since an error can occur at this time, it differs from the time when measurement actually starts tens of seconds to1 minute.

1. Select measurement.
2. Specify time to the **Job Start Time** input box.

Fig. 2.66 Input of measurement start time

2.20.8 Measurement Information

If you double-click on the experiment displayed on the **Spectrometer Control** window, the **Job Info** window that displays information about measurement opens.

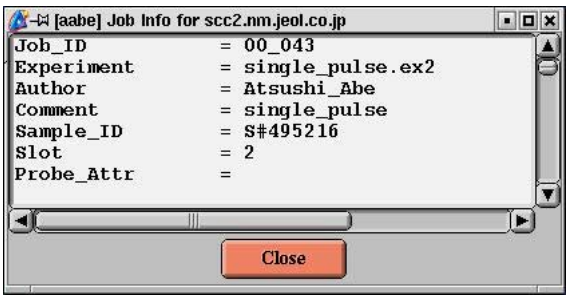

Fig. 2.67 Job Info

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2.21 APPENDIX

2.21.1 Probe Tuning

The tuning method of the TH5AT/FG2 probe will be explained as an example.
When turning on the power supply of the auto-tuning unit, the TH5AT/FG2 probe can be tuned automatically.
When turning off the power supply of the auto-tuning unit, and removing the flexible shaft, the TH5AT/FG2 probe tuning can be performed as follows.

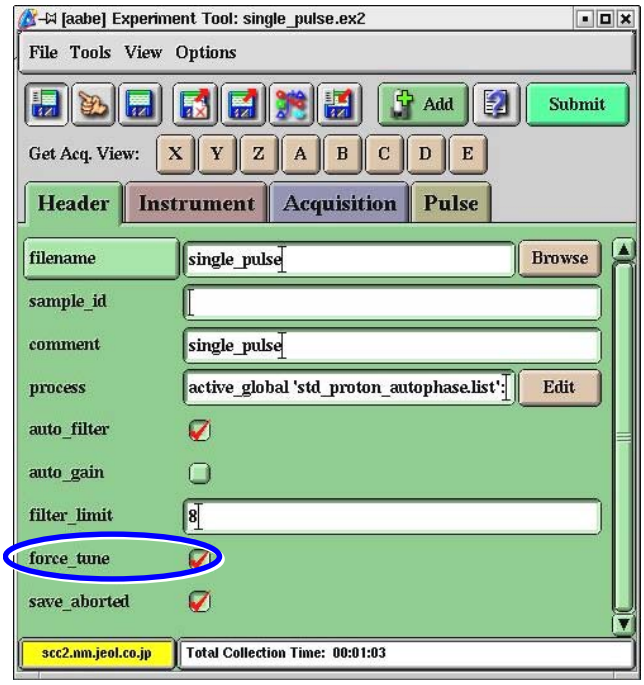
■ ^{1}H tuning in normal measurement

● To set the ^{1}H measurement conditions

1. Click on the **Expmnt** button in the **Delta Console** window.
   The **Open Experiment** window appears.
2. Click on the **Global Directory** button.
   The contents of the **Global Experiment** directory are displayed.
3. Click on the measurement mode **single_pulse.ex2** to highlight it.
4. Click on the **Ok** button.
   The **Experiment Tool** window appears.
5. Set each parameter for normal ^{1}H measurement in sequence in the **Header, Instrument, Acquisition,** and **Pulse** sections in the **Experiment Tool** window.

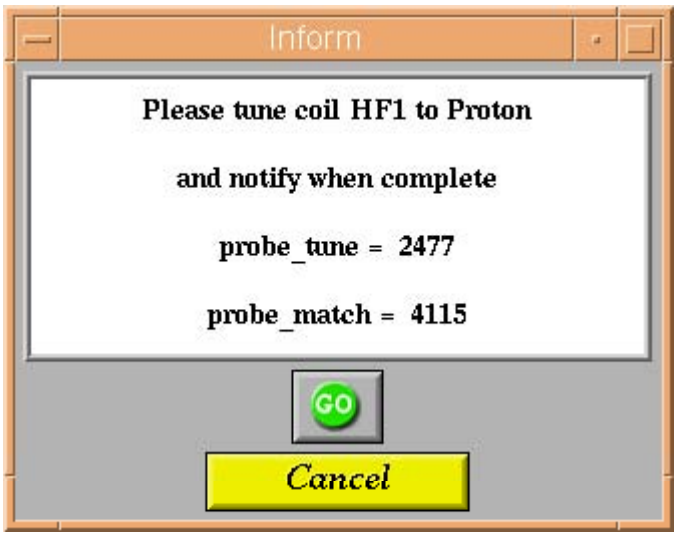
● Tuning the probe

1. Click on the **force_tune** check box (☑) in the **Header** section.



2. Click on the **Submit** button.

The tuning message is displayed as shown below. At this time, the probe has already been set to tuning.



3. Set the tuning sensitivity.

If the **LEVEL METER** on the head amplifier chassis moves too much or too little, adjust the sensitivity using the **METER GAIN** button and knob.

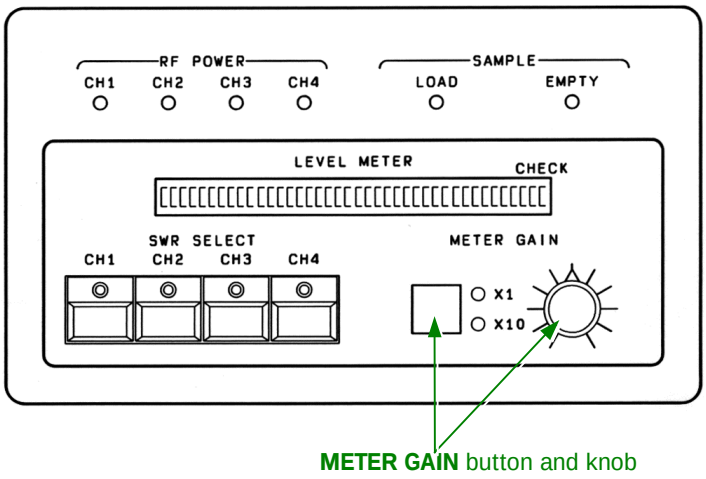


Fig. 2.68 Display panel of the head amplifier chassis

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4. To tune the probe, minimize the deflection of **LEVEL METER**. Adjust first the **HF1 TUNE** dial of the probe, and next the **HF1 MATCH** dial. Finally, readjust the **HF1 TUNE** dial.

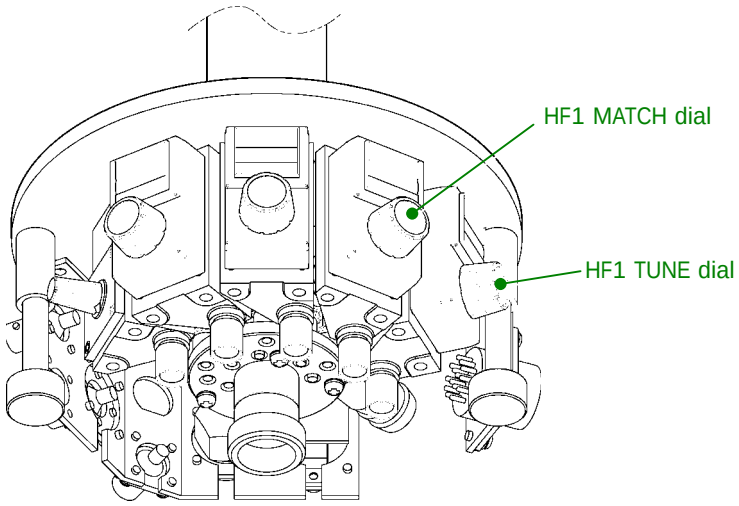


Fig. 2.69 Automatic-tuning 5 mm FG NMR tunable probe

5. On completion of tuning, click on the **GO** button to start normal ^{1}H measurement.

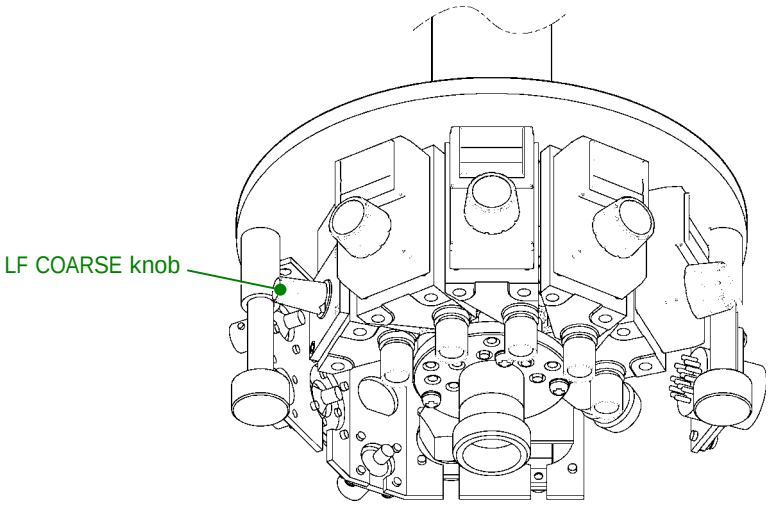
^{13}C tuning in normal measurement

To set the ^{13}C measurement conditions

1. Click on the **Expmnt** button in the **Spectrometer Control** window.
   The **Open Experiment** window appears.
2. Click on the **Gloval Directory** button.
   The contents of the **Global Experiment** directory are displayed.
3. Click on the measurement mode **single_pulse_dec.ex2** to highlight it.
4. Click on the **Ok** button.
   The **Experiment Tool** window appears.
5. Set each parameter for normal ^{13}C measurement in sequence in the **Header, Instrument, Acquisition,** and **Pulse** sections in the **Experiment Tool** window.

To tune the probe

1. Set the **LF COARSE** knob of the probe to the ^{13}C frequency range.
   For the values of tuning and matching dials for the observation nucleus, refer to the table provided with the TH5AT/FG2 probe.



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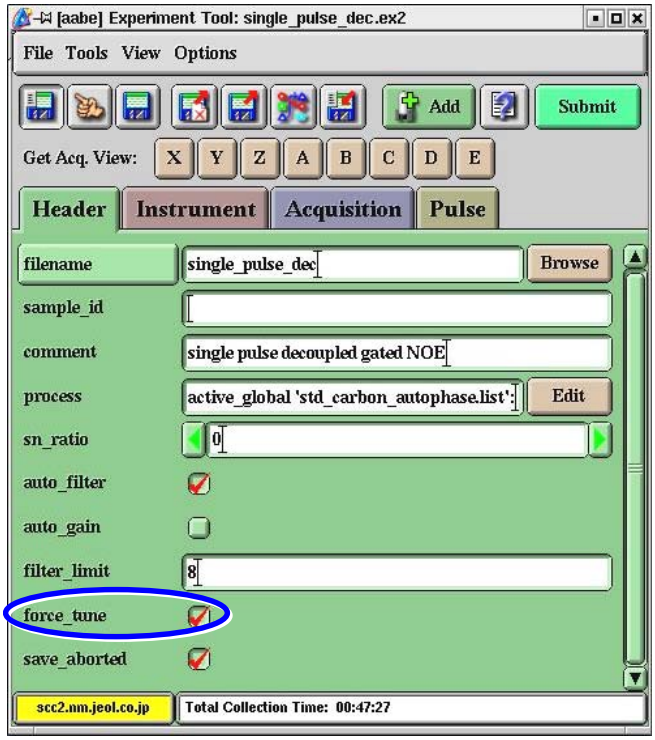
2. Click on the **force_tune** check box (☑) in the **Header** section.

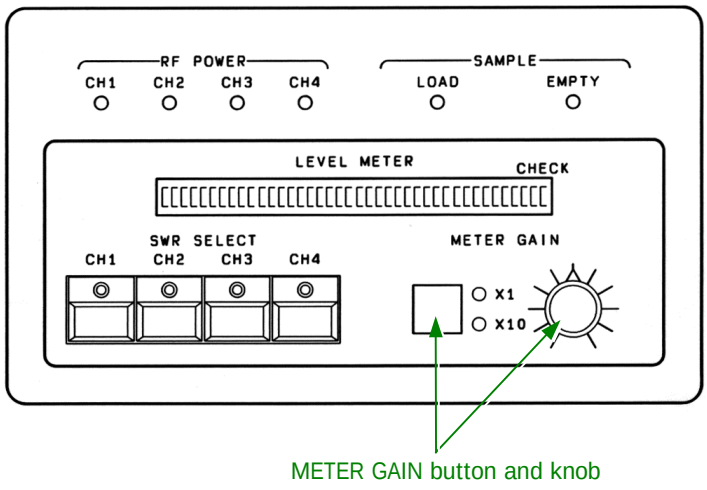


3. Click on the **Submit** button.

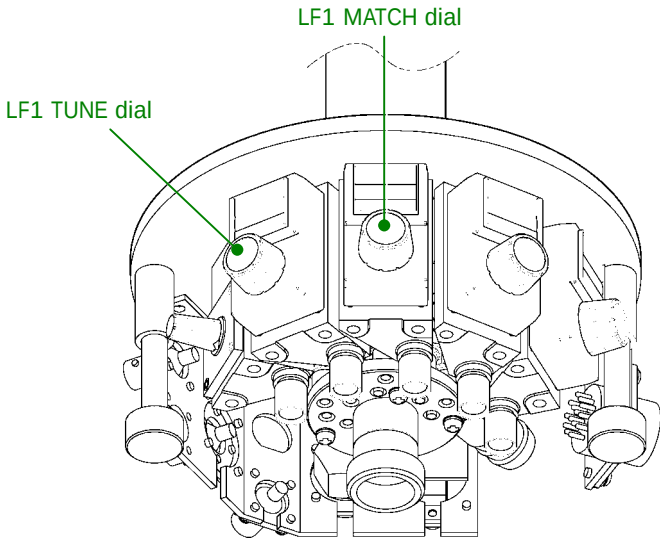
The tuning messages are displayed. First, the ^{13}C tuning message is displayed.

4. Set the sensitivity of tuning.

If the **LEVEL METER** on the head amplifier chassis moves too much or too little, adjust the sensitivity using the **METER GAIN** button and knob.

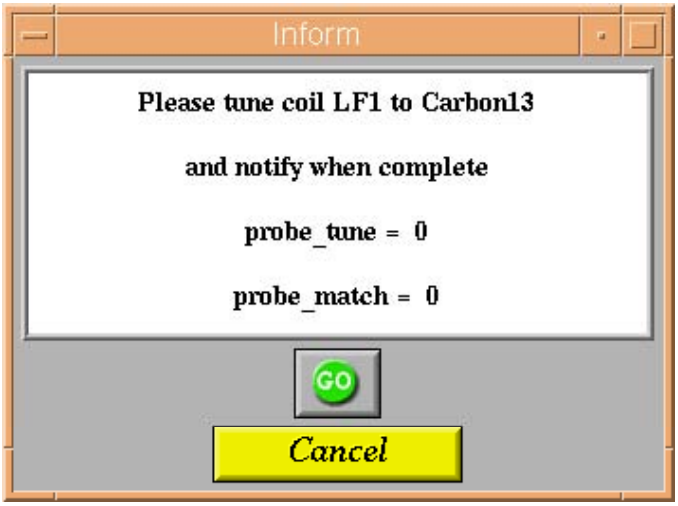


5. To tune the probe, minimize the deflection of **LEVEL METER**. Adjust first the **LF1 TUNE** dial of the probe, and next the **LF1 MATCH** dial. Repeat these operations until no further improvement results.



6. On completion of tuning, click on the **GO** button.

After the ^{13}C tuning is complete, the ^{1}H tuning message appears. At this time the probe has already been set to tuning.



7. Perform the ^{1}H tuning.

8. On completion of ^{1}H tuning, click on the **GO** button to start normal ^{13}C measurement.

C I

Precise ^{13}C tuning

1. Turn the **LF1 MATCH** dial to minimize the deflection of **LEVEL METER**.
2. Turn the **LF1 TUNE** dial to minimize the deflection of **LEVEL METER**.
3. Turn the **LF1 MATCH** dial by +10 graduations and turn the **LF1 TUNE** dial to minimize the deflection (F1) of **LEVEL METER**.
   Memorize the deflection (F1) of **LEVEL METER** at that time.
4. Turn the **LF1 MATCH** dial by –10 graduations and turn the **LF1 TUNE** dial to minimize the deflection (F2) of **LEVEL METER**.
   Compare the deflection (F2) of **LEVEL METER** at this time with F1. Turn the **LF1 MATCH** dial to minimize the deflection of **LEVEL METER**, and then turn the **LF1 TUNE** dial to minimize the deflection of **LEVEL METER**.

2.21.2 Array Measurement

When you perform array measurement, there are parameters whose values are changed in some order. They are called the array parameters.

This section describes the methods of setting the array parameters in the **Experiment Tool** window. Array measurement can be carried out in the same way as ordinary measurement by clicking on the **Submit** button.

There are the two methods of setting the array parameters as described below:

- Entering a numerical value into the parameter input box directly
- Using the array parameter window

Array parameter notation

Most of measurement parameters can be used as array parameters using the **y_acq** command for 1D measurement. The character **y** indicates that the array parameters form the temporary **y_domain** of 2D data sets.
The array parameters for **2**D measurement are also represented as **z_acq**, and form the temporary **z_domain** of 3D data sets.

This section describes array measurement in the ***single_pulse.ex2*** window.

☞ For explanation about Array data processing, refer to the Processing User's Manual.

■ Preparation before setting array parameters

1. Select the measurement mode from the **Open Experiment** window, and click on the **Ok** button.
   The **Experiment Tool** window opens.
2. Enter the parameters, such as **filename** and **sample_id**.

C I

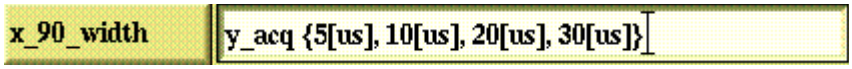
Entering a numerical value into the parameter input box directly

The format for input into the parameter input box is

y_acq{value1, value2, value3.....}

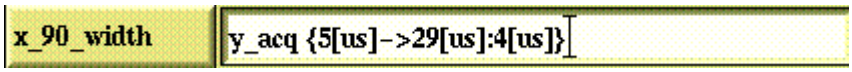
Array parameter values enclosed with braces { } follow **y_acq**, and allow any numerical values or numerical values varying with a constant difference.

Example: **x_90_width** parameters



To enter numerical values varied with a constant interval in a range, the format is

y_acq{start value ->stop value : step size}



To enter a parameter having a unit, enter the unit with at least one numerical value.
If you specify only one unit, the unit is applied to all numerical values.

At the end of input, press the Enter key or move the mouse pointer outside the window. If an error is detected in the array parameters, a message is displayed.

To change the numerical values in the parameter input box, move the mouse pointer into the input box, and correct them using the arrow keys or the backspace key.

To enter a long array, scroll the end of the window. To return to the beginning after scrolling, use the Home or End key.

You can use both **y_acq** and **z_acq** simultaneously. In this case, first, the **y_acq** array is executed using the **z** parameter values, then the **y_acq** array is executed with the increment of the **z** parameter, and these steps are repeated, resulting in pseudo 3D data.

Using the array parameter window

The procedure for setting the **scans** parameter is described as an example.

1. Double-click on the **scans** button of the **Experiment Tool** window.
   The array parameter window opens.

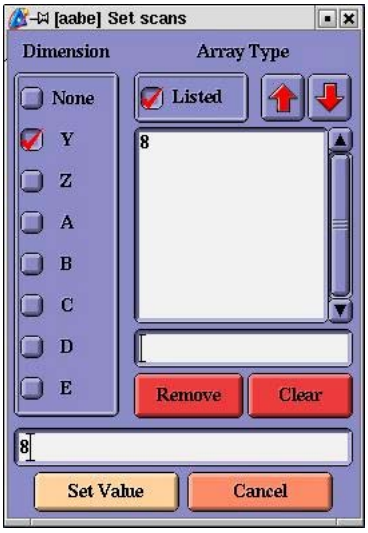
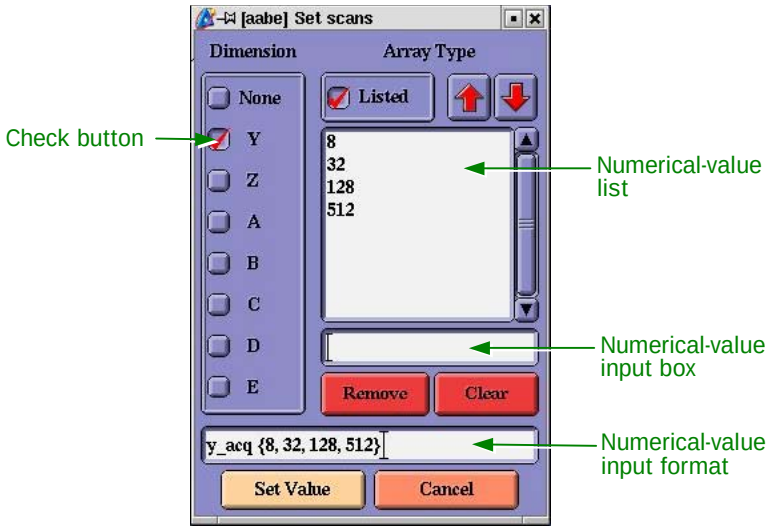
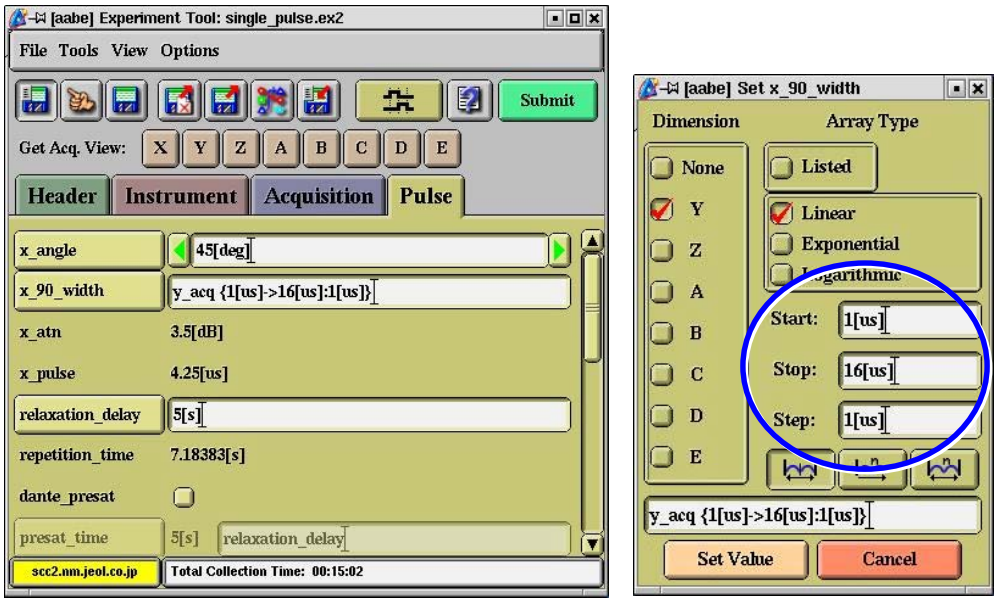


Fig. 2.70 Array parameter window

2. Select the **Y** check button by clicking on it.
3. Enter the parameter values one by one into the numerical input box.

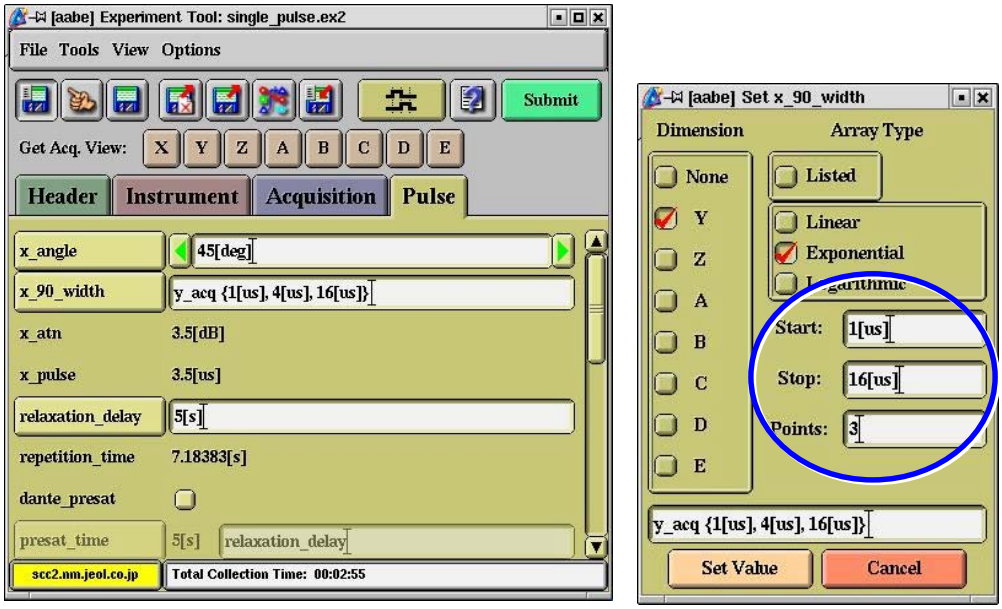


4. To enter the values in a range, click on the **Listed** check button to turn it off.
5. Select **Array Type** from **Linear**, **Exponential**, and **Logarithmic**.
   The example of **x_90_width** parameters is shown below.



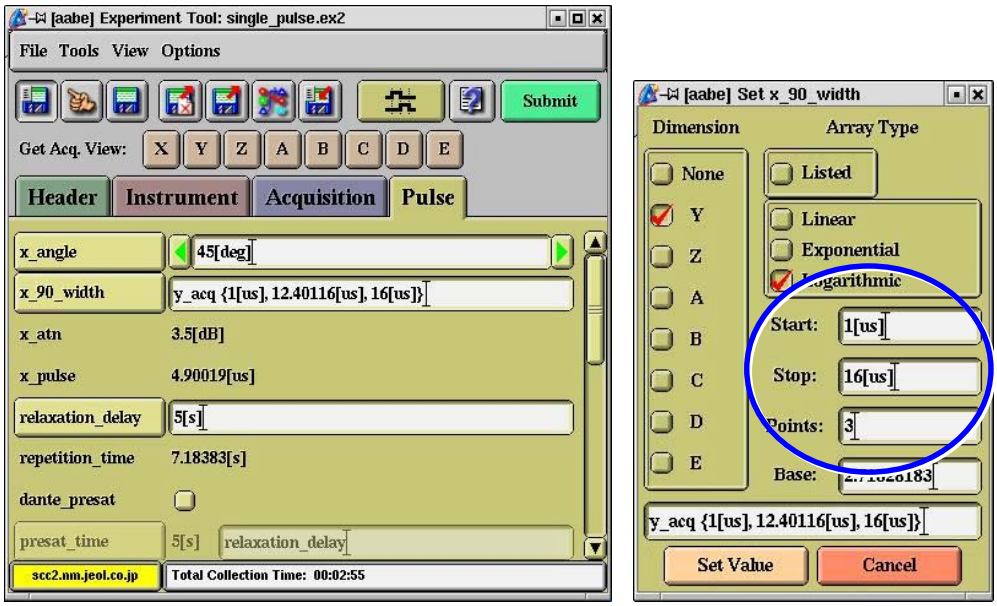
Selecting Linear

If you select **Linear**, enter the values of **Start, Stop,** and **Step** in the input boxes. In the above example, the parameter varies linearly from 1[us] to 16[us] with a 1[us] interval, that is, 1, 2, 3.....14, 15, and 16 [us] (16 points in total).



Selecting Exponential

If you select **Exponential**, enter the values of **Start, Stop,** and **Points** in the input boxes. In the above example, the parameter varies exponentially from 1[us] to 16[us] with the three-point interval, that is, 1, 4, and 16 [us].

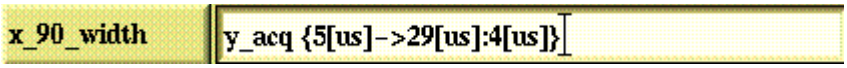


Selecting Logarithmic

If you select **Logarithmic**, enter the values of **Start, Stop,** and **Points** in each input box. In the above example, the parameter varies **l**ogarithmically from 1[us] to 16[us] with the three-point interval, that is, 1, 12.40116, and 16 [us].

6. Click on the **Set Value** button.

The following figure shows the setting of the parameter input box in the **Experiment Tool** window.



- **Reference: The method of entering numerical values from the geometry into the array parameters window**

You can enter the numerical values from the data (geometry) displayed on the screen into the array parameters window.

The procedure is explained using the **irr_offset** parameter as an example.

1. Select **Pick–Copy position to buffer** from the cursor tool bar.

2. Move the mouse pointer onto the spectrum displayed on the screen, and click the left mouse button on the peak set to **irr_offset.**

The peak position is copied.

3. Move the mouse pointer to the numerical value input box in the array parameters window, and click on the middle mouse button.

The copied position is pasted, and the numerical value is entered into the list box.

4. Repeat the copy and paste operation, and enter the numerical values into the list box.

- You can perform array measurement only if the array parameter window opens when you click on the item.
- You cannot use the parameters related to the size of files and the sampling points as the array parameters, for example, **domains, sweep widths**, and **points**.

  If you want to change these parameters and perform successive measurements, use the ordinary queue.

3

ADJUSTMENT OF NMR PARAMETERS

The greatest feature of the pulsed NMR method is that various informations can be derived from spectra which are affected by applying combinations of pulses (pulse sequences). The nuclear magnetization can be controlled by the pulsed RF excitation. To manipulate the magnetization precisely, you must set the parameters for controlling the magnetization. Chapter 3 explains the procedures for these operations.

3.1 PURPOSE OF MEASURING PULSE WIDTHS 3-1

3.2 SPECTROMETER RF SYSTEM AND FACTORS AFFECTING PULSE WIDTHS 3-3

3.3 MEASUREMENT OF PULSE WIDTHS WHEN OUTPUT IS USED AT HALF POWER 3-5

3.4 CALCULATION OF 90° PULSE WIDTHS AFTER THE ATTENUATOR VALUE IS CHANGED 3-8

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3.6 CALCULATION OF 90° PULSE WIDTH OF SELECTIVE EXCITATION PULSES 3-10

3.7 USAGE OF Attenuator Calculator TOOL 3-12

3.1 PURPOSE OF MEASURING PULSE WIDTHS

This section explains the significance and principle of measurement of pulse widths, and general precautions.

About pulse width

When an RF pulse having the magnetic-field strength $\boldsymbol{B_1}$ is applied to the magnetization M in a rotating frame, the magnetization will precess about the axis along the direction of the applied RF pulse with the angular velocity $\gamma \boldsymbol{B_1}$ (rad/s), where γ is the magnetogyric ratio.

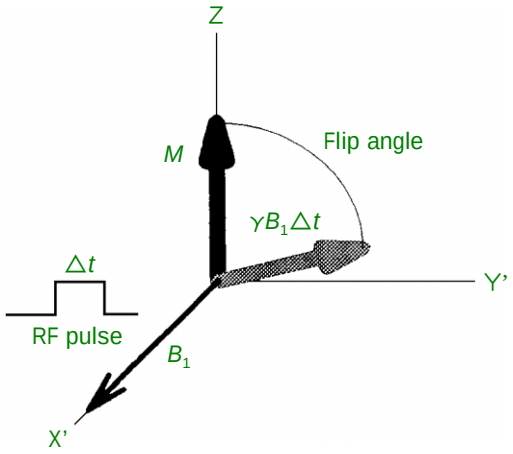

Fig. 3.1 Precession of magnetization in the rotating frame

As a consequence, if the RF pulse width (the duration of the RF pulse) is $\triangle t$ (s), the magnetization after the pulse is then related to the magnetization after the pulse by the flip angle thus:

Flip angle = $\gamma \boldsymbol{B_1} \triangle t$ (rad)

In the NMR terminology, the RF pulse width resulting in a flip angle X° is called the X° pulse width, and the pulse itself the X° pulse.

To carry out precise NMR measurement, it is essential for you to know the magnetic-field strength of the RF pulse. However, in the pulsed NMR spectrometer, it is more convenient to use the 90° pulse width $\boldsymbol{PW_{\pi/2}}$ than to use the field strength $\boldsymbol{B_1}$ directly, so that when the magnetic field strength of the RF pulse is referred to, generally $\boldsymbol{PW_{\pi/2}}$ is used. If $\mathbf{PW}_{\pi/2}$ is known, $\boldsymbol{B_1}$ can be computed by the following equation:

$$\boldsymbol{B_1} = \pi / (2 \times \gamma \times \boldsymbol{PW_{\pi/2}})$$

Principle of measurement of pulse widths

The saturation magnetization is a vector parallel to the Z axis. If the saturation magnetization is $\boldsymbol{M_0}$, and after the RF pulse with width $\triangle$t and strength $\boldsymbol{B_1}$ is applied to the saturation magnetization, the observed signal intensity is

$$\boldsymbol{M}(\triangle t) = \boldsymbol{M_0} \sin(\gamma \boldsymbol{B_1} \triangle t)$$

Thus, the 90° pulse width is the value of $\triangle$t at which the signal intensity becomes a maximum when $\triangle$t is gradually increased. However, in practice, it is much easier to find the position where the signal intensity becomes zero, so first find the 180° pulse

width and then estimate the 90° pulse width as half its duration, or first find 360° pulse width and then estimate the 90° pulse width as one fourth of its duration.

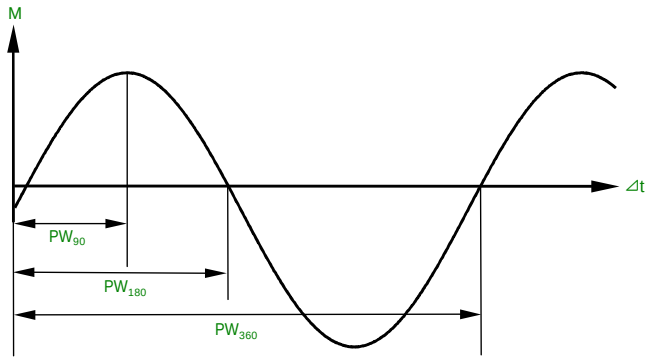

Fig. 3.2 Relationship between the time the RF pulse is applied and the observed signal intensity

Effects of inhomogeneity of the RF magnetic field strength B_1

In the previous paragraph, it was assumed that the homogeneous RF magnetic field $\boldsymbol{B}_1$ was applied to the entire sample. In practice, however, depending on the shape of the coil for generating the RF magnetic field and the sample position relative to the coil, RF magnetic fields having various strengths are applied to the sample. As a result, the observed signal intensity is not a simple sinusoidal function of the duration of the RF pulse. Therefore, more accurate value can be obtained by finding 360° pulse width and then estimating the 90° pulse width as one fourth of its duration.

3.2 SPECTROMETER RF SYSTEM AND FACTORS AFFECTING PULSE WIDTHS

In order to adjust the power of the RF pulse or to measure the pulse width, it is necessary for you not only to learn the procedure for measurement but also to understand the flow of RF pulses in the spectrometer. You can understand the meaning of the measurement procedure from understanding the flow of the RF pulses. This section describes the flow of the RF pulses in the spectrometer and various factors affecting the pulse widths.

■ Outline of the spectrometer RF system

In order to help you to understand the operation of the pulse sequence, a simplified schematic diagram of the RF system in the spectrometer is shown in Fig. 3.3.

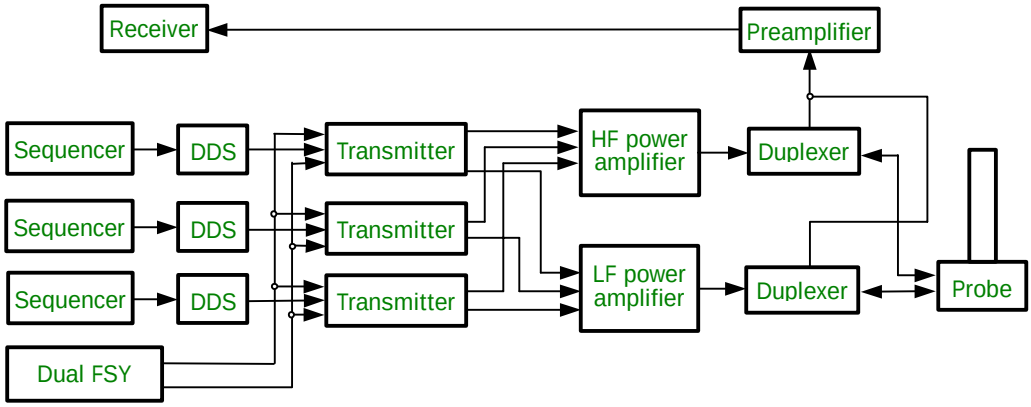

Fig. 3.3 Block diagram of the RF system

The standard probe provided with the spectrometer is a tunable double-resonance probe. This probe can be tuned to the ^{1}H resonance frequency and the resonance frequencies of nuclei in the range from ^{31}P to ^{15}N. The channel into which RF power at the ^{1}H frequency is entered is called the HF (High Frequency) channel, and the other channel the LF (Low Frequency) channel. Do not confuse the HF and LF channels with the observation and irradiation channels. The HF or LF channel from which a signal at the frequency of an nucleus being observed is output is called the observation channel. The other channel is called the irradiation channel.

The signals output from the sequencer are converted to pulses in the DDS. After they are modulated, they enter into the transmitter. At the same time, the pulses from the dual FSY enter the transmitter, and are mixed there to produce the RF pulses. The intensity of the RF pulses can be changed in 1 dB steps by the amplitude control in the DDS, and in 0.01 dB steps by the attenuator in the transmitter, allowing very fine adjustment. When you enter a value in the **attenuator** box, the attenuation can automatically be adjusted by the above devices, so usually you do not care about them. The RF pulses output from the transmitter are entered into either the HF or the LF power amplifier. The RF pulses are amplified in the power amplifier, and are entered into the corresponding channel in the probe. The host computer selects the HF or the LF channel as the observation channel. The strong RF pulses are applied to the observation channel through the duplexer. After the strong RF pulses are switched off, the weak observation signals are received by the probe. The signal from the probe is amplified in the preamplifier, and reaches the receiver. The RF pulses are also applied to the irradiation channel through the duplexer.

When the RF pulses are output, the spectrometer automatically selects the sequencer to use. The output power differs a little, depending on the selected sequencer, but its error is less than 3 %, and is negligible in actual measurement. Therefore, measure only the pulse width when observation is carried out. You do not need to measure the pulse width when irradiation is carried out. Also, when you change the RF power using the attenuator, you can compute a pulse width because of its good linearity.

Factors affecting the pulse width

The pulse width is determined by the strength of the RF magnetic field applied to the sample. The strength of the RF magnetic field is determined by the shape of the RF coil and the current running through the coil. The shape of the RF coil is a characteristic of the probe. However, the current running through the RF coil depends on various factors. By understanding these factors, it is possible to consider when the pulse width should be measured, and what points attention should be paid to for performing precise measurement.

The electric current running through the RF coil depends mainly on the following four factors:

(a) Design of the probe tuning circuit
(b) State of the tuning circuit
(c) Susceptibility of the sample
(d) Power output by the power amplifier

The factor (a) is a characteristic of the probe. The factor (b) varies with the frequency of the RF pulse, room temperature, and sample temperature, and with (c) susceptibility of the sample. When the state of the tuning circuit changes, it can be corrected to a certain extent by retuning the probe, and returned to near the optimum condition. However, when the sample has a large susceptibility, it is impossible to return it completely to the same conditions even if the probe is tuned. The factor (d) varies for many reasons. The output of the analog power amplifier may change with time. It also depends on temperature, which influences the transistors in the power amplifier. Generally, the output increases with a decrease in temperature. It is also frequency-dependent. Signals entered into the power amplifier are most likely influenced by temperature and elapsed time as well.

Pulse widths to be adjusted or measured

Precise pulse widths have been preset in the spectrometer at the time of installation. However, they may change due to various conditions. When they change, adjust or measure the following pulse widths:

- Pulse width when you use output at half power
- Pulse width when you change an attenuator value
- Pulse width when you measure DEPT90
- Pulse width of selective excitation pulse

☞ For information on how to measure or calculate these pulse widths, refer to the sections that follow.

3.3 MEASUREMENT OF PULSE WIDTHS WHEN OUTPUT IS USED AT HALF POWER

The NMR spectrometer contains a power amplifier having sufficient output power. The output at full power is too strong, so usually half power, using the attenuator at 3 dB, is used for measurement. This section explains the method of measuring a pulse width at half power, supposing you can operate basic ^{1}H and ^{13}C 1D NMR measurement and data processing.

■ Attenuators

The maximum output of the power amplifier in the NMR spectrometer is so strong that normally the attenuators are used to reduce the intensity of RF signals. The parameters that specify the ratios of attenuation represent attenuator values. The parameter of the attenuator in each channel is shown in the following table.

Channel name	Parameter name
Observation channel	**x_atn**
Irradiation channel	**irr_atn**

The attenuator values are in the range from 0 to 120 dB. The full power is output at 0 (zero) dB and the minimum power at 120 dB. When the attenuator value increases by 3 dB, the input power into the power amplifier decreases by half according to the following equation:

$$Pow2 / Pow1 = 10^{-0.1\times(ATT2-ATT1)}$$

where
*Pow*1: Power when the attenuator value is *ATT*1
*Pow*2: Power when the attenuator value is *ATT*2

The magnetic field strength $\boldsymbol{B}_1$ produced by the RF coil is proportional to the voltage applied to the coil. This voltage is proportional to the square root of the power. The relationship between the attenuator value and the RF magnetic field strength $\boldsymbol{B}_1$ is expressed by the following equation as long as the amplification factor is linear.

$$\boldsymbol{B}_{1\_2} / \boldsymbol{B}_{1\_1} = 10^{-0.1\times(ATT2-ATT1)/2}$$

where
$\boldsymbol{B}_{1\_1}$: Magnetic field strength when the attenuator value is *ATT*1
$\boldsymbol{B}_{1\_2}$: Magnetic field strength when the attenuator value is *ATT*2

The pulse width is inversely proportional to $\boldsymbol{B}_1$. Thus,

$$\boldsymbol{PW}_{90\_2} / \boldsymbol{PW}_{90\_1} = 10^{+0.1\times(ATT2-ATT1)/2}$$

where
$\boldsymbol{PW}_{90\_1}$: 90° pulse width when the attenuator value is *ATT*1
$\boldsymbol{PW}_{90\_2}$: 90° pulse width when the attenuator value is *ATT*2

For example, to double the pulse width, increase the attenuator value by approximately 6 dB.

✍ Decibel (dB)
The number of decibels denotes the ratio of the two amounts of energy or amplitudes of waves such as electromagnetic waves and sound waves. A decrease in energy by 10 dB, for example, means that the energy becomes one tenth of its previous value. A decrease in amplitude by 20 dB means that the amplitude becomes one tenth of its previous value.

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■ Measuring 90° pulse width in the observation channel

As explained in Section 3.1, first obtain the 360° pulse width, and then estimate the 90° pulse width as one fourth of its value. In practice, obtain the 90° pulse width according to the following procedure.

1. Insert a standard sample or a desired sample into the probe.

When you want to measure a pulse width under normal conditions, use the standard sample. When you want to measure a pulse width under special conditions, such as at high temperature, or using a special solvent, select a sample which can be measured under the same conditions.

2. Carry out tuning.

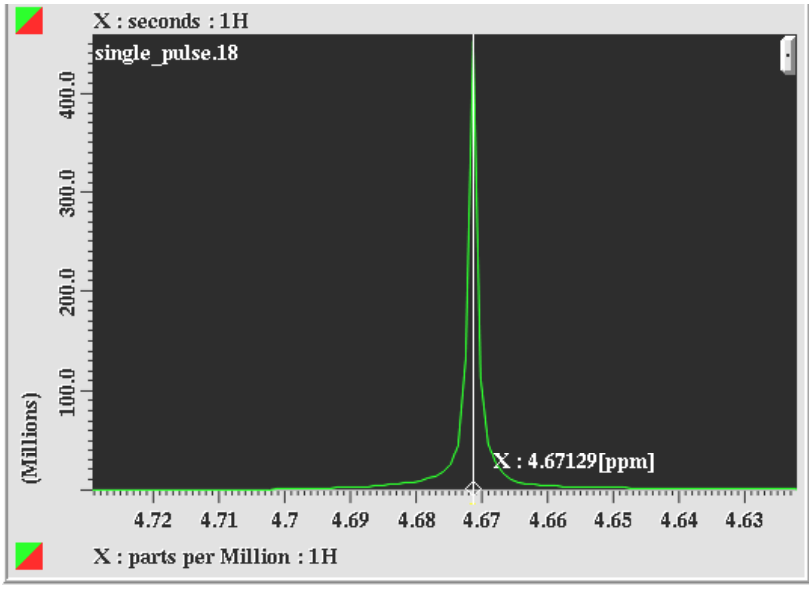
3. Enhance the resolution.

4. Observe ^{1}H spectra using **single_pulse.ex2**, or observe ^{13}C spectra using ***single_pulse_dec.ex2.***

5. Set a peak which can be used as a mark to the center of the observation range.

☞ Select as the mark a broad peak having a relatively short relaxation time. If the relaxation time is too long, you may not obtain the 90° pulse successfully.

a. Select **Copy position to buffer** from the Cursor Tool **Pick** mode, and click on the top of the mark peak to copy it.



b. Click the middle mouse button on **x_offset** parameter in the measurement mode to paste the copied position on it.

6. Set **x_angle** to **90** deg.

7. Set **x_90_width** to Array measurement.

8. Click on the **Submit** button.

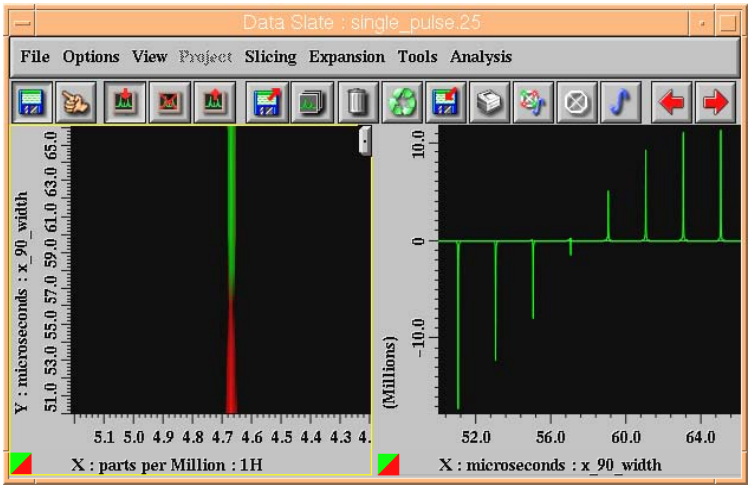
The pulses are generated, starting measurement.

✍ If the **Inform** window appears, click on the **GO** button.

9. Carry out the **Linearize** processing on the obtained data.

10. Find the pulse width whose signal intensity is nearest to zero.

The pulse width at which the signal intensity of the linearized spectrum is nearest to zero is the 360° pulse width. As the pulse widths become longer, the peaks should turn upward.


Data Slate : single_pulse.25
File Options View Project Slicing Expansion Tools Analysis
Y : microseconds : x_90_width
51.0 53.0 55.0 57.0 59.0 61.0 63.0 65.0
5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.
X : parts per Million : 1H
(Millions)
10.0
0
-10.0
52.0 56.0 60.0 64.0
X : microseconds : x_90_width

11. Obtain the 90° pulse width by dividing the 360° pulse width by four.

Take note of the obtained 90° pulse width together with the measurement conditions.

■ Measuring pulse widths in the irradiation channel

The NMR spectrometer has been adjusted so that the pulse width does not change regardless of whether it is set in the observation channel or in the irradiation channel, as long as their frequencies are the same. Therefore, you need not measure the pulse width in the irradiation channel.

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3.4 CALCULATION OF 90° PULSE WIDTHS AFTER THE ATTENUATOR VALUE IS CHANGED

Some measurement modes require a change in the intensity of the RF pulse during the pulse sequence. If you change the intensity of the RF pulse, you need to measure the pulse width again, as it varies. However, because the RF power in the NMR spectrometer has good linearity, you can obtain the pulse width simply by calculation as described below.

■ To calculate the pulse width from the attenuator value

When you change the attenuator value, you can obtain the pulse width according to the following equation.

$$PW_{90\_2} = PW_{90\_1} \times 10^{0.1\times(ATT2-ATT1)/2}$$

where
$\boldsymbol{PW}_{90\_1}$: 90° pulse width when the attenuator value is $ATT1$
$\boldsymbol{PW}_{90\_2}$: 90° pulse width when the attenuator value is $ATT2$

For example, when the RF power is half power, that is, the attenuator value is $ATT1$ = 3 dB, and the 90° pulse width is $\boldsymbol{PW}_{90\_1}$ = 12 μs, the 90° pulse width for the attenuator value $ATT2$ = 15 dB is given by

$$PW_{90} = 12 \times 10^{0.1\times(15-3)/2} = 24 \ [\mu s]$$

■ To calculate the attenuator value from the pulse width

The attenuator value can also be determined from the pulse width according to the following equation.

$$ATT2 = ATT1 + 20 \times \log_{10} \frac{PW_{90\_2}}{PW_{90\_1}}$$

Where
$\boldsymbol{PW}_{90\_1}$: 90° pulse width when the attenuator value is $ATT1$
$\boldsymbol{PW}_{90\_2}$: 90° pulse width when the attenuator value is $ATT2$

For example, when the RF power is half power, that is, the attenuator value is $ATT1$ = 3 dB, and the 90° pulse width is $\boldsymbol{PW}_{90\_1}$ = 12 μs, the attenuator value for the 90° pulse width $\boldsymbol{PW}_{90\_2}$ = 24 μs is given by

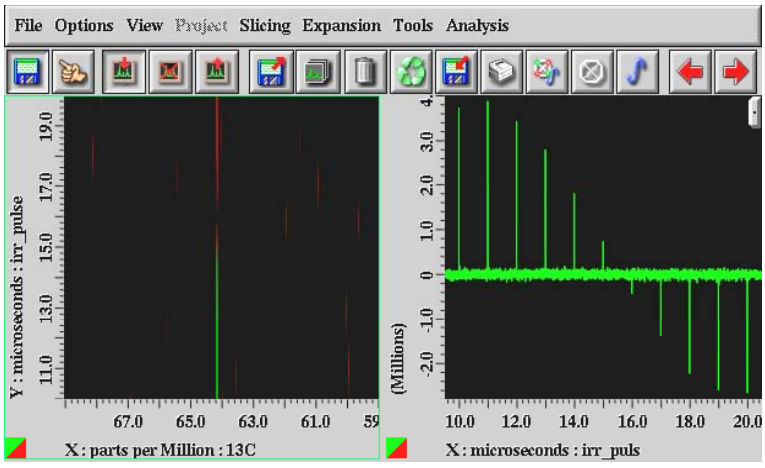
$$ATT = 3 + 20 \times \log_{10} \frac{24}{12} = 9 \ [dB]$$

3.5 MEASUREMENT OF PULSE WIDTHS IN DEPT90

To eliminate both CH_2 and CH_3 in DEPT effectively, inhomogeneity of $\boldsymbol{B}_1$ affects the pulse width. Therefore, the procedure in Section 3.3 cannot be used to measure the 90° pulse width. Instead, in DEPT90, measure the 90° pulse width according to the following procedure.

■ Measuring 90° pulse width in DEPT90 measurement

1. Prepare a ^{13}C standard sample with as high as possible a concentration of $-CH_2$, and insert it in the probe.
2. Tune the probe.
3. Enhance the resolution.
4. Set the measurement mode to **dept.ex2**.
5. Set **selection_angle** to **90** deg.
6. Set **irr_pulse** for Array measurement.
   ✍ The approximate value for carrying out Array measurement is 10 to 15 μs when a TH5 probe is used.
7. Click on the **Submit** button.
   The pulses are generated, starting measurement.
   ✍ If the **Inform** window appears, click on the **GO** button.
8. Carry out the **Linearize** processing on the obtained data while watching the $-CH_2$ signal.
9. Find the pulse width so that the signal intensity is nearest to zero.
   The pulse width at which the signal intensity of the linearized processed spectrum is nearest to zero is the 90° pulse width. As the pulse widths become longer, the peak should turn downward.



☞ Take note of the obtained 90° pulse width together with the measurement conditions.

C I

3.6 CALCULATION OF 90° PULSE WIDTH OF SELECTIVE EXCITATION PULSES

In the NMR spectrometer, the 90° pulse widths of selective excitation pulses can be obtained according to the following calculation.

■ To calculate 90° pulse widths of selective excitation pulses

The 90° pulse widths of selective excitation pulses can be calculated in the same way as normal pulse widths.

$$PW_{90\_2} = \frac{PW_{90\_1} \times 10^{0.1\times(ATT2-ATT1)/2}}{\alpha}$$

where
$\boldsymbol{PW}_{90\_1}$: 90° pulse width when the attenuator value is $ATT1$
$\boldsymbol{PW}_{90\_2}$: 90° pulse width when the attenuator value is $ATT2$
α: Coefficient depending on the waveform shown in the following table

Waveform	α
rectangle	1
gauss	0.41064
sinc	0.587191
sin	0.634135
SEDUCE	0.469984
e-burp1	0.067093
e-burp2	0.061043
u-burp1	0.024613
i-burp1	0.149611
i-burp2	0.100649
re-burp	0.079805

For example, when the RF power is half power, that is, the attenuator value is $ATT1$ = 3 dB, and the 90° pulse width is $\boldsymbol{PW}_{90\_1}$ = 12 μs, the 90° pulse width with the Gaussian waveform for the attenuator value 9 dB is given by

$$PW_{90} = \frac{12\times10^{0.1\times(9-3)/2}}{0.41064} = 58.3\ [\mu s]$$

To calculate the attenuator value from the pulse width

On the other hand the attenuator value can be determined from the pulse width according to the following equation.

$$ATT2 = ATT1 + 20 \times \log_{10}\left(\alpha \times \frac{PW_{90\_2}}{PW_{90\_1}}\right)$$

where
$\boldsymbol{PW}_{90\_1}$: 90° pulse width when the attenuator value is $ATT1$
$\boldsymbol{PW}_{90\_2}$: 90° pulse width when the attenuator value is $ATT2$

For example, when the RF power is half power, that is, the attenuator value is $ATT1$ = 3 dB, and the 90° pulse width is $\boldsymbol{PW}_{90\_1}$ = 12 μs, the attenuator value for the 90° pulse width of 200 μs with the Gaussian waveform is given by

$$ATT = 3 + 20 \times \log_{10}\left(0.41064 \times \frac{200}{12}\right) = 19.7 \ \ [dB]$$

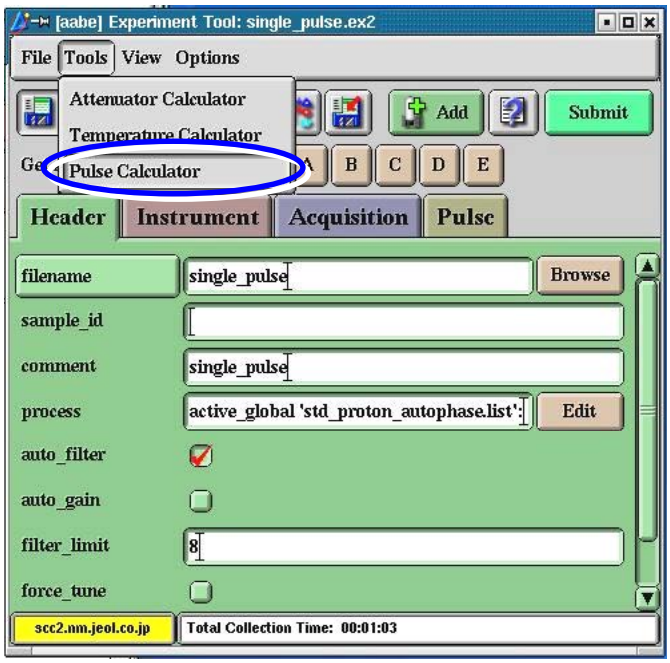
C I

3.7 USAGE OF PULSE CALCULATOR TOOL

The Delta software includes the **Pulse Calculator** tool. You can calculate a pulse width from an attenuator value and vice versa using this tool. This section explains how to use it.

■ Starting Pulse Calculator tool

◆ Select **Tools**–**Pulse Calculator** from the **Experiment Tool** window.



The **Pulse Calculator** window opens.

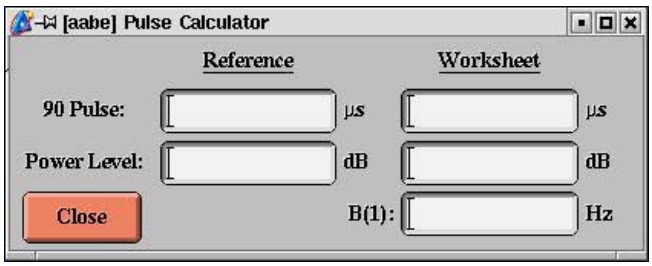


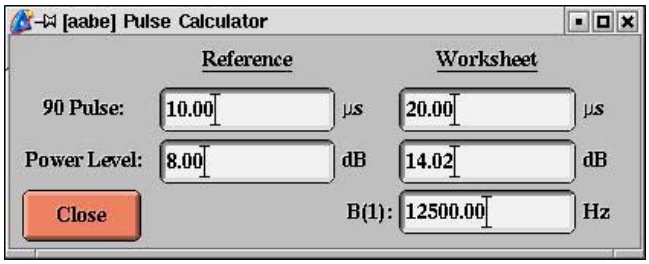
Fig. 3.4 Pulse Calculator window

■ Using the Pulse Calculator tool

For example, when 90° pulse width which attenuator value is 8 dB is 10 μs, in order to calculate the attenuator value for 90° pulse width of 20 μs, carry out following operation.

1. Input 10 μs to **90 Pulse** of **Reference**.
2. Input 8 dB to **Power Level** of **Reference**.

3. Input 20 μs to **90 Pulse** of **Worksheet**.
Calculation result is displayed in **Power Level** of **Worksheet** and **B(1)**.



4

USAGE OF PULSE SEQUENCES

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STYLE OF DESCRIPTION

This chapter explains various types of NMR measurement in the following format.

Header xxxxx.ex2

The header indicates the name of an experiment file.
The directory in which the files are located is shown under the experiment filename.

✍ The measurement mode, standard values of measurement parameters, and data processing steps are stored in the experiment file (.exp).

☞ For information on directories, refer to the Supplementary notes, “Directory tree structure.”

■ Purpose

The purpose of measurement is briefly described.

■ Pulse sequences

The pulse sequences used for this measurement are illustrated schematically.
The correspondence between the parameters and the timing of pulses is also shown.

■ Extension sequences

The function of extension sequences from which you can select, for example, decoupled or non-decoupled measurement, is shown.

■ Parameters

The parameters to be set before measurement is carried out, their meanings, and default values or recommended initial values are shown.
Some of the initial values are set as defaults stored in a probe file.

x90	90° pulse width of the observation channel
spin_lock_90	90° pulse width of the spin locking (MLEV-17 sequence)
attenuator	Attenuator value of the observation channel in spin locking
y90_hi	90° pulse width of the irradiation channel

These values are adjusted for individual probes.

■ Data processing

The name of the process list which is to be loaded after the measurement is complete is indicated.
These process lists are located in the global directory, **/usr/delta/global/process_list**.

■ How to interpret the spectrum

Briefly describes how to interpret and analyze the spectrum obtained using this measurement method.

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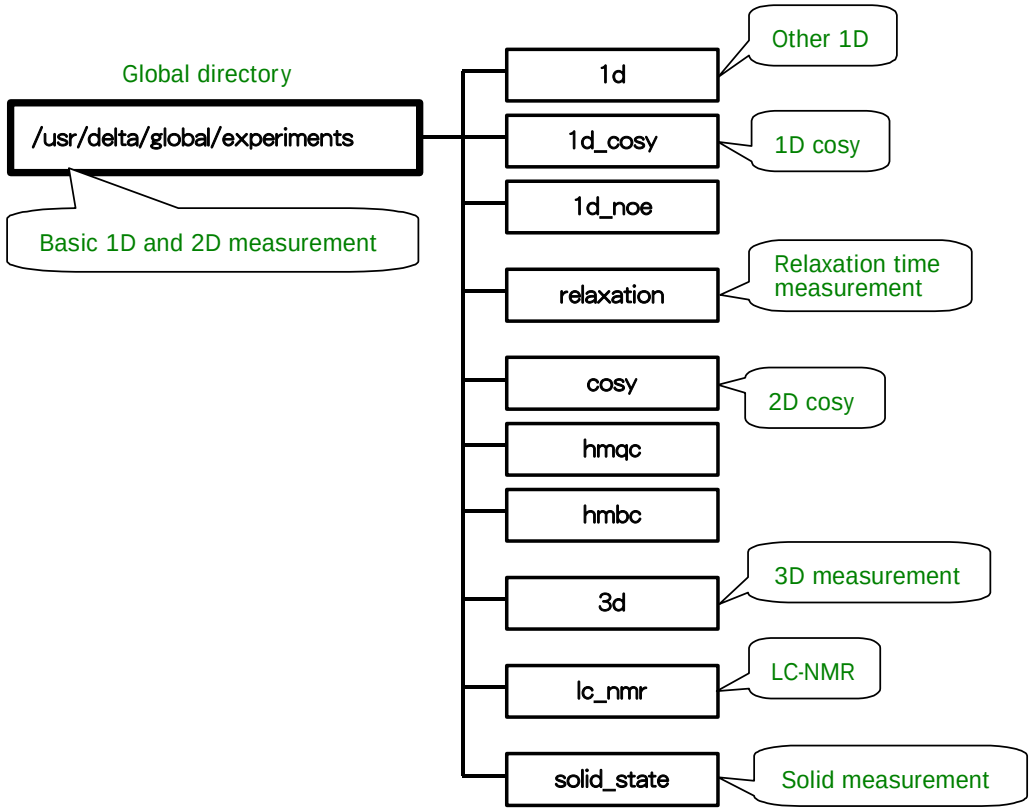
Supplementary notes

Brief remarks regarding measurement, and parameters to be adjusted.

✍ Directory tree structure
Individual experiment files are stored in the directories.
The directories and files form a tree structure as shown in the figure below.



Directory tree structure

C I

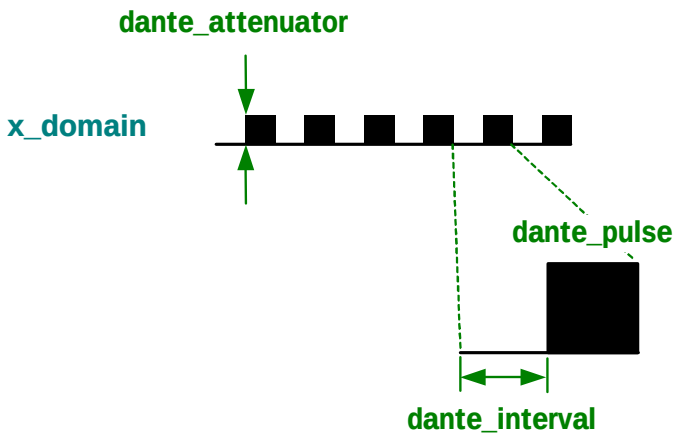
4.1 EXTENSION SEQUENCES

The concept of extension sequences is used for each sequence used in the NMR spectrometer. For example, to use presaturation to eliminate a solvent signal in a single-pulse experiment, select **Presaturation** from the extension functions in the sequence of **single_pulse.ex2.** This section explains the purpose and parameters of these extension sequences which are used in common in the individual sequences.

4.1.1 dante_presat

Dante presaturation reduces a signal that would overwhelm the desired peak, such as a water signal in an aqueous-solution sample, making it easy to detect the sample signal.

■ Pulse sequences



■ Parameters

presat_time Duration of presaturation. The default is the same as **relaxation_delay.**
Take care not to set a time longer than **relaxation_delay.**

dante_pulse Dante pulse width. The default is **2 us**.

dante_interval Dante pulse interval. The default is **100 us**.

dante_attenuator Determines RF output for the dante pulse. The default is **40 dB**. Every time 3 dB is added, the RF output is halved.

dante_loop Indicates number of repetitions of the dante pulse.

■ Supplementary note

Dante presaturation eliminates a signal from the observation center. It is appropriate for eliminating a very strong solvent signal such as one from light water.

C I

4.1.2 Presaturation

Presaturation reduces a signal that would overwhelm the desired peak, such as a water signal in an aqueous-solution sample, making it easy to detect the sample signal.

Parameters

irr_domain (**tri_domain**)

The irradiation nucleus is set to the same as the observation nucleus.

irr_offset (**tri_offset**)

Irradiation position (resonance frequency of peak to irradiate). The default is **5 ppm**.

irr_attenuator (tri_attenuator)

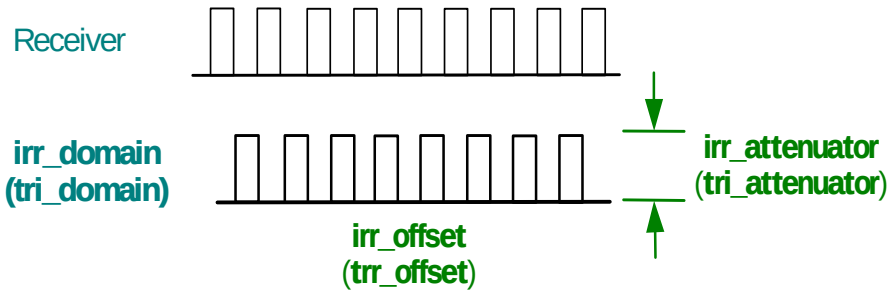
Determines RF output for the irradiation pulse for presaturation. The default is **40 dB**. Every time 3 dB is added, the RF output is halved.

C I

4.1.3 Homo Decouple

Used to perform homonuclear spin-spin decoupling.

Pulse sequences



Parameters

irr_domain (tri_domain)

The irradiation nucleus is set to the same as the observation nucleus.

irr_offset (tri_offset)

Resonance frequency of the peak to be irradiated. The default is **5 ppm**.

irr_attenuator (tri_attenuator)

Determines RF output for spin decoupling pulses. The default is **40 dB**. Every time 3 dB is added, the RF output is halved.

Supplementary note

The multiple splitting of a peak due to spin coupling to the irradiated peak is eliminated by decoupling. Thus, the peaks having spin-spin coupling with each other can be determined.

C I

4.1.4 noe

The NOE (Nuclear Overhauser Effect) arises from carrying out irradiation in the irradiation channel during waiting time, enhancing the S/N ratio.

Parameters

irr_atn_noe Determines RF output for NOE irradiation. The default is the attenuator value to which **irratn_lo** is set in the probe file. Every time 3 dB is added, the RF output is halved.

noe_time NOE irradiation time. The default is the same as **relaxation_delay**.

irr_pwidth Pulse width for NOE irradiation. The default is the pulse width **irr90_hi** set in the probe file.

irr_domain Irradiation nucleus. The default is **Proton**.

irr_offset Irradiation position (resonance frequency of the peak to be irradiated). The default is **5 ppm**.

irr_noise Decoupling mode. The default is **WALTS**.

C I

4.1.5 decoupling

Used to perform heteronuclear spin-spin decoupling.

Parameters

irr_atn_dec Determines RF output for decoupling. The default is the attenuator value to which **irratn_hi** is set in the probe file. Every time 3 dB is added, the RF output is halved.

irr_pwidth Pulse width of the decoupling pulse. The default is the pulse width **irr90_hi** set in the probe file.

irr_domain Irradiation nucleus. The default is **Proton**. However, in some cases, such as when it is the same nucleus as **y_domain**, there is no input box.

irr_offset Resonance frequency of the peak to be irradiated. The default is **5 ppm**. However, in some cases, such as when it is the same as **y_offset**, there is no input box.

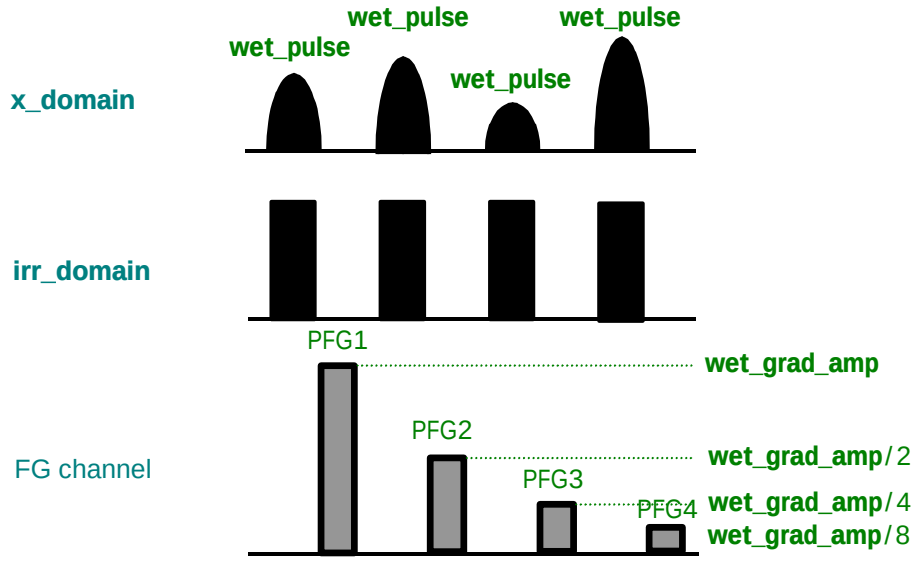
irr_noise Decoupling mode. The default is **WALTS**.

C I

4.1.6 wet_suppression

This WET sequence is used to reduce a signal that would overwhelm the desired peak, such as a water signal in an aqueous-solution sample.

Pulse sequences



Parameters

wet_pulse Pulse width of the shaped pulse to be used for WET sequences. The default is **10 ms.**

wet_attenuator Determines RF output for the shaped pulse to be used for WET sequences. The default is **58.2 dB**. Every time 6 dB is added, the pulse width is halved.

wet_offset Resonance frequency of a peak to be WET irradiated. The default is equal to **x_offset**.

wet_shape Waveform of the shaped pulse. The default is **seduce**.

wet_grad Pulse width of the PFG pulse. The default is **2 ms**.

wet_grad_amp Output of the PFG pulse. The default is **48%.**

wet_grad_shape Waveform of the PFG pulse. The default is **SQUARE**.

wet_grad_recover Recovery time after the PFG pulse. The default is **0.1 ms**.

irr_domain Irradiation nucleus. The default is **Carbon13**.

irr_offset Resonance frequency of the peak to be irradiated. The default is **50 ppm**.

irr_pwidth Pulse width **irr90_hi** of the decoupling pulse that is set in the probe file.

irr_noise Decoupling mode. The default is **CW**.

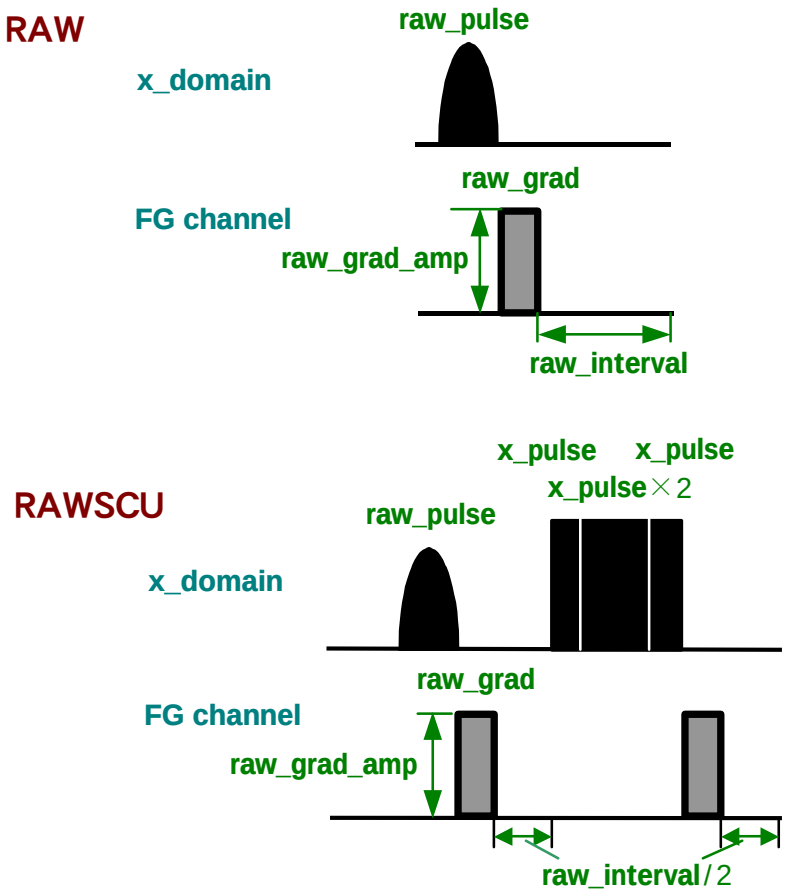
irr_atn_dec Determines RF output for decoupling. The default is the attenuator value **irratn_hi** set in the probe file. Every time 3 dB is added, the RF output is halved.

C I

4.1.7 raw_suppression

This RAW/RAWSCUBA sequence is used to reduce a signal that would overwhelm the desired peak, such as a water signal in an aqueous-solution sample.

■ Pulse sequences



■ Parameters

raw_pulse Pulse width of the shaped pulse used for the RAW sequence. The default is the pulse width **x90_soft** set in the probe file.

raw_attenuator Determines RF output for the shaped pulse in the RAW sequence. The default is the attenuator value **xatn_soft** set in the probe file. Every time 6dB is added, the pulse width is halved.

raw_shape Select the waveform of the shaped pulse. The default is **GAUSS**.

raw_grad Pulse width of the PFG pulse. The default is **1 ms**.

raw_grad_amp Output of the PFG pulse. The default is **38.4%.**

raw_grad_shape Waveform of the PFG pulse. The default is **SQUARE**.

raw_interval Pulse interval in the RAW sequence. The default is **100 ms**.

C I

4.2 1D MEASUREMENT

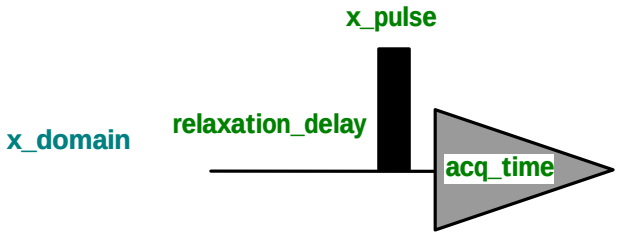
4.2.1 single_pulse.ex2

Simplest single-pulse measurement
Directory: **/usr/delta/global/experiments/1d**

Purpose of measurement

To carry out measurement using a single pulse sequence.

Pulse sequences



Extension sequences

dante_presat	The default is **FALSE**.
irr_mode	Select **Off**, **Presaturation**, or **Homo Decouple**. The default is **Off**.
tri_mode	Select **Off**, **Presaturation**, or **Homo Decouple**. The default is **Off**.

Parameters

x_domain	Observation nucleus. The default is **Proton**.
x_offset	Observation center. The default is **5 ppm**.
x_sweep	Observation range. The default is **15 ppm**.
x_points	Number of points to sample. The default is **16K**.
scans	Number of scans to accumulate. The default is **8** scans**.**
x_prescans	Number of dummy scans.
x_90_width	90° pulse width. The default is **x90** set in the probe file.
x_angle	Flip angle. The default is **45 deg**.
x_atn	The attenuator value **xatn** set in the probe file. Every time 6 dB is added, the pulse width is halved.
x_pulse	Pulse width computed as

$$\textbf{x\_90\_width} \times \frac{\textbf{x\_angle}}{90°}$$

relaxation_delay	Waiting time between repeated pulses. The default is **5 s**.
repetition_time	**relaxation_delay** + **x_acq_time**.

Data processing

The standard process list is **std_proton_autophase.list**.

C I

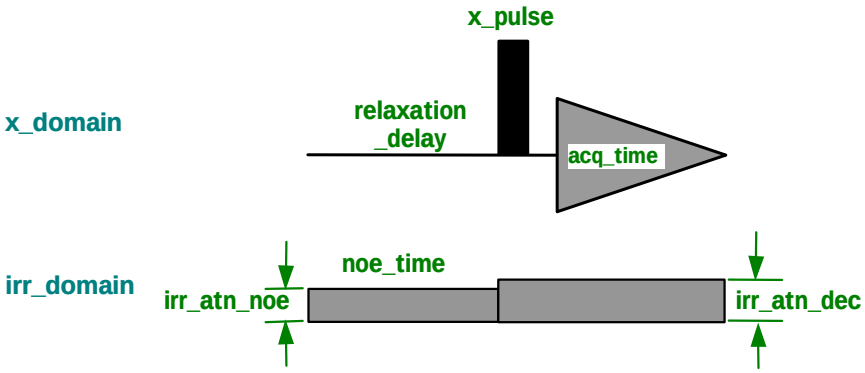
4.2.2 single_pulse_dec.ex2

Single-pulse measurement with heteronuclear decoupling.
Directory: **/usr/delta/global/experiments/1d**

Purpose of measurement

To carry out measurement using a single-pulse sequence with heteronuclear decoupling.

Pulse sequences



Extension sequences

noe The default is **TRUE**.

decoupling The default is **TRUE**.

Parameters

x_domain Observation nucleus. The default is **Carbon13**.

x_offset Observation center. The default is **100 ppm**.

x_sweep Observation range. The default is **250 ppm**.

x_points Number of points to sample. The default is **32K**.

scans Number of scans to accumulate. The default is **1000** scans.

x_prescans Number of dummy scans.

x_90_width 90° pulse width. The default is **x90** set in the probe file.

x_angle Flip angle. The default is **30 deg**.

x_atn The attenuator value **xatn** set in the probe file.

x_pulse Pulse width computed as

$$\textbf{x\_90\_width} \times \frac{\textbf{x\_angle}}{90^\circ}$$

relaxation_delay Waiting time between repeated pulses. The default is **2 s**.

repetition_time **relaxation_delay**+ **x_acq_time**.

Data processing

The standard process list is **std_carbon_autophase.list**.

C I

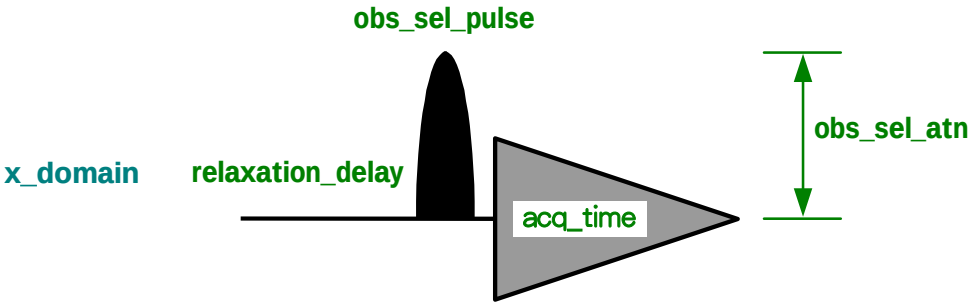
4.2.3 single_pulse_shape.ex2

Single-pulse measurement using shaped pulses
Directory: **/usr/delta/global/experiments/1d**

Purpose of measurement

To set the 90° shaped pulse width when **obs_sel_atn** is used.

Pulse sequences



Extension sequences

dante_presat	The default is **FALSE**.
irr_mode	Select **Off**, **Presaturation**, or **Homo Decouple**. The defaul is **Off**.
tri_mode	Select **Off**, **Presaturation**, or **Homo Decouple**. The defaul is **Off.**

Parameters

x_domain	Observation nucleus. The default is **Proton**.
x_offset	Observation center. The default is **5 ppm**.
x_sweep	Observation range. The default is **15 ppm**.
x_points	Number of points to sample. The default is **16K**.
scans	Number of scans to accumulate. The default is **16** scans.
x_prescans	Number of dummy scans.
obs_sel_pulse	90° pulse width of the shaped pulse. The default is the pulse width **x90_soft** set in the probe file.
obs_sel_atn	Determines RF output for the selective-excitation pulse. The default is the attenuator value **xatn_soft** set in the probe file. Every time 6 dB is added, the pulse width is halved.
obs_sel_shape	Waveform of the selective-excitation pulse. The default is **GAUSS**.
relaxation_delay	Waiting time between repeated pulses. The default is **5 s**.
repetition_time	**relaxation_delay**+ **x_acq_time**.

Data processing

The standard process list is **std_proton.list**.

C I

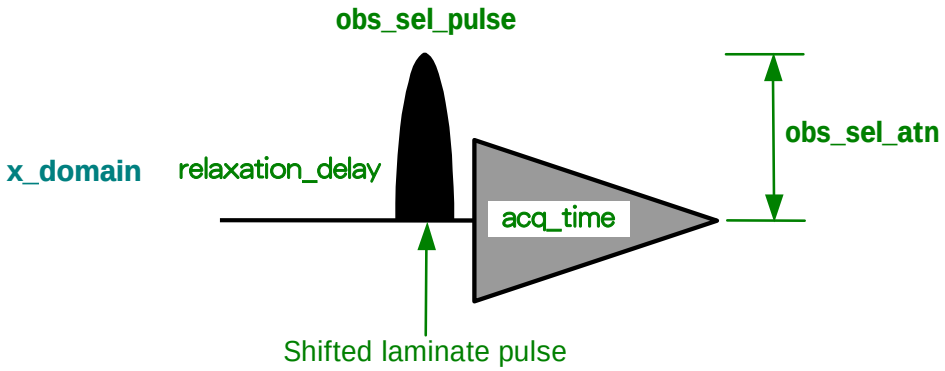
4.2.4 single_pulse_shape_slp.ex2

Selective-excitation measurement using shifted laminate pulses
Directory: **/usr/delta/global/experiments/1d**

Purpose of measurement

To set the 90° shifted laminate pulse width when **obs_sel_atn** is used to adjust the RF output.

Pulse sequences



Extension sequences

dante_presat	The default is **FALSE**.
irr_mode	Select **Off**, **Presaturation**, or **Homo Decouple**. The default is **Off**.
tri_mode	Select **Off**, **Presaturation**, or **Homo Decouple**. The default is **Off**.

Parameters

x_domain	Observation nucleus. The default is **Proton**.
x_offset	Observation center. The default is **5 ppm**.
x_sweep	Observation range. The default is **15 ppm**.
x_points	Sampling points. The default is **16K**.
scans	Number of scans to accumulate. The default is **16** scans.
x_prescans	Number of dummy scans.
obs_sel_pulse	90° pulse width of the shaped pulse. The default is the pulse width **x90_soft** set in the probe file.
obs_sel_atn	Determines RF output for the selective-excitation pulse. The default is the attenuator value **xatn_soft** set in the probe file. Every time 6 dB is added, the pulse width is halved.
obs_sel_shape	Waveform of the selective-excitation pulse. The default is **GAUSS**.

C I

slp_number Number of peaks to be irradiated by the laminate pulse (up to six). The default is 1.

slp_offset1 Resonance frequency of the peak to be irradiated by the laminate pulse. The default is **5 ppm**.

slp_offset2 (slp_offset2, slp_offset3, slp_offset4, slp_offset5, slp_offset6)
Resonance frequencies of the peaks (two or more peaks) to be irradiated by the laminate pulse. The default is **0 ppm**.

obs_sel_shape Waveform of the selective-excitation pulse. The default is **GAUSS**.

obs_shape_slp Position to be irradiated by the laminate pulse. The default is **5 ppm**.

relaxation_delay Waiting time between repeated pulses. The default is **5 s**.

repetition_time **relaxation_delay+ x_acq_time**.

Data processing

The standard process list is **std_proton.list**.

Supplementary note

A shift laminate pulse allows excitation of multiple frequencies by applying rf intensity and phase modulation to the pulse with a specific waveform.

C I

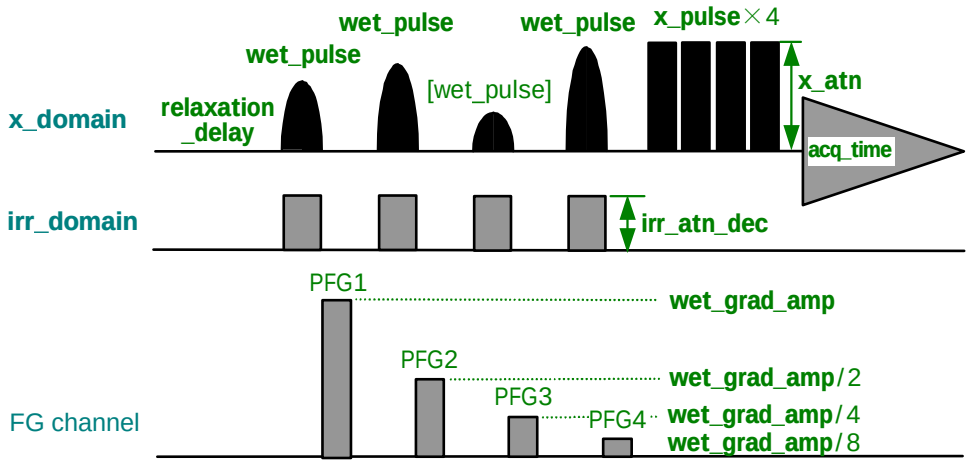
4.2.5 single_pulse_wet.ex2

Single-pulse measurement including the WET sequence
Directory: /usr/delta/global/experiments/1d

Purpose of measurement

To reduce a signal that would overwhelm the desired signal, such as a water signal in an aqueous-solution sample, using the WET sequence.

Pulse sequences



Extension sequences

wet_suppression	The default is **TRUE**.
dante_presat	The default is **FALSE**.
tri_mode	Select **Off**, **Presaturation**, or **Homo Decouple**. The default is **Off**.

Parameters

x_domain	Observation nucleus. The default is **Proton**.
x_offset	Observation center. The default is **5 ppm**.
x_sweep	Observation range. The default is **15 ppm**.
x_points	Number of points to sample. The default is **16 K**.
scans	Number of scans to accumulate. The default is **16** scans.
x_prescans	Number of dummy scans.
x_pulse	90° pulse width **x90** set in the probe file.
x_atn	Attenuator value **xatn** set in the probe file. Every time 6 dB is added, the pulse width is halved.
relaxation_delay	Waiting time between repeated pulses. The default is **5 s**.
repetition_time	**relaxation_delay**+ **x_acq_time**.

Data processing

The standard process list is **std_proton.list**.

C I

4.2.6 apt.ex2

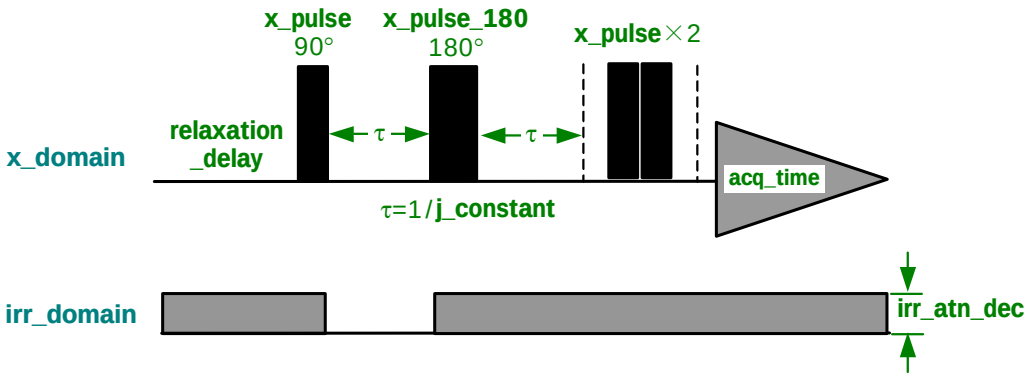
APT measurement
Directory: /usr/delta/global/experiments/1d

✍ APT is the abbreviation of Attached Proton Test.

Purpose of measurement

To determine the number of hydrogen nuclei directly bonded to each carbon nucleus.

Pulse sequences



Parameters

x_domain Observations nucleus. The default is **Carbon13**.

x_offset Observation center. The default is **100 ppm**.

x_sweep Observation range. The default is **250 ppm**.

x_points Number of points to sample. The default is **32K**.

scans Number of scans to accumulate. The default is **1000 times**.

x_prescans Number of dummy scans.

x_angle Flip angle. The default is **45 deg**.

x_90_width 90° pulse width. The default is **x90** set in the probe file.

x_pulse Pulse width computed as

$$\mathbf{x\_90\_width} \times \frac{\mathbf{x\_angle}}{90°}$$

x_pulse_180 Indicates 180° pulse width **x_90_width** ×**2**.

x_atn Attenuator value **xatn** set in the probe file. Every time 6 dB is added, the pulse width is halved.

j_constant Value of $^{1}J_{CH}$. The default is **140 Hz**.

relaxation_delay Waiting time between repeated pulses. The default is **1 s.**

repetition_time **relaxation_delay**+ **x_acq_time.**

C I

irr_domain	Irradiation nucleus. The default is **Proton**.
irr_pwidth	Pulse width **irr90_hi** of the decoupling pulse that is set in the probe file.
irr_offset	Irradiation center. The default is **5 ppm**.
irr_noise	Decoupling pulse mode. The default is **WALTZ**.
irr_atn_dec	Determines RF output for decoupling. The default is the attenuator value **irratn_hi** set in the probe file. Every time 3 dB is added, the RF output is halved.

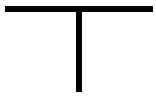
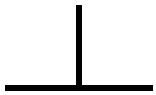
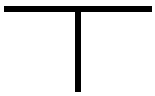
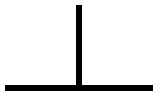
Data processing

The standard process list is **std_apt.list**.

How to interpret the spectrum

The appearances and features of signals for the multiplicity of resonance lines are shown below.

Appearance of signal patterns

Multiplicity of the resonance lines			
>C< (Singlet)	−CH< (Doublet)	—CH_2— (Triplet)	−CH_3 (Quartet)
			

C I

4.2.7 dept.ex2

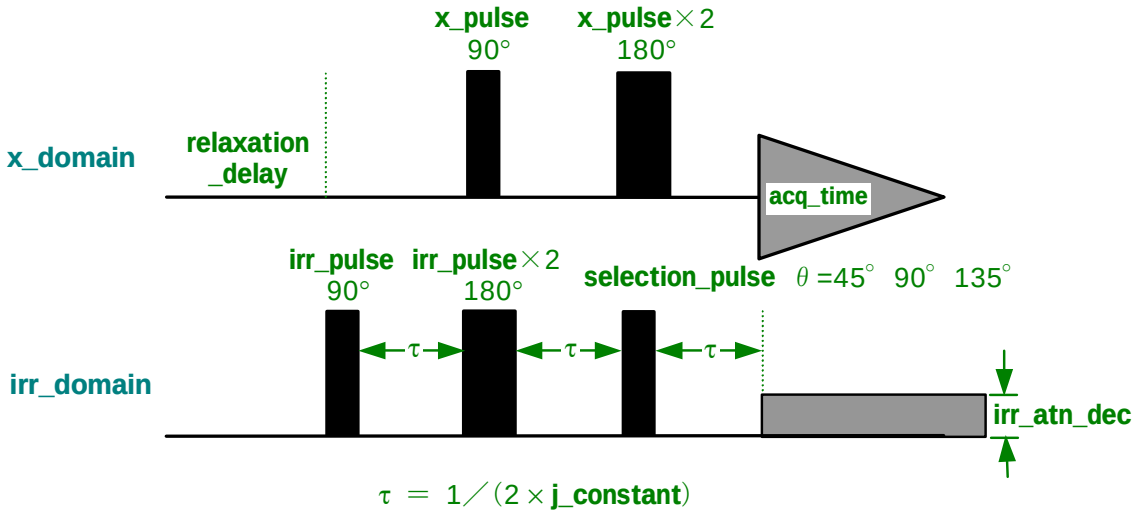
DEPT measurement
Directory: /usr/delta/global/experiments/1d

✍ DEPT is the abbreviation of nuclear Distortionless Enhanced by Polarization Transfer.

■ Purpose

This pulse sequence is used to determine the number of hydrogen nuclei directly coupled to each carbon nucleus.
This method provides an enhancement of the sensitivity by polarization transfer from a ^{1}H nucleus to a ^{13}C nucleus, and by repetition of the pulses after the ^{1}H relaxation time, the measurement time can significantly be reduced compared with the off-resonance method. Spectral additions and subtractions can be performed to edit spectra because the phase shift is less than that in the INEPT method. However, the signal of quaternary carbon does not appear.

■ Pulse sequence



■ Extension sequences

decoupling The default is **FALSE**.

■ Parameters

x_domain Observation nucleus. The default is **Carbon13**.

x_offset Observation center. The default is **100 ppm**.

x_sweep Observation range. The default is **250 ppm**.

x_points Number of points to sample. The default is **32K**.

scans Number of scans to accumulate (a multiple of eight). The default is 1000 times.

x_prescans Number of dummy scans.

C I

x_pulse	90° pulse width in the ^{13}C observation channel. The default is **x90** set in the probe file.
x_atn	Determines RF output. The default value is **xatn** set in the probe file. Every time 6 dB is added, the pulse width is halved.
irr_domain	Irradiation nucleus. The default is **Proton**.
irr_offset	Irradiation center. The default is **5 ppm**.
irr_pulse	90° pulse width in the ^{1}H irradiation channel. The default is **irr90** set in the probe file.
irr_atn	Determines RF output in the irradiation channel. The default is **irratn** set in the probe file. Every time 6 dB is added, the pulse width is halved.
selection_angle	Flip angles (45°, 90°, or 135°) of the irradiation pulse. The default is **45 deg**.
selection_pulse	The pulse width in the irradiation channel. It is computed as $$\textbf{irr\_pulse} \times \frac{\textbf{selection\_angle}}{90°}$$
j_constant	Value of $^{1}\mathbf{J_{CH}}$. The default is **140 Hz**.
relaxation_delay	Waiting time (1-5 s) between repeated pulses. This value is 4 –5 s for molecular weights about 300. It is about 2 s for higher molecular weights.
repetition_time	**relaxation_delay+ x_acq_time**.

Data processing

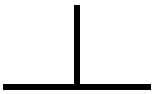
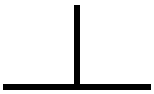
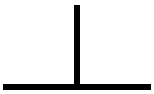
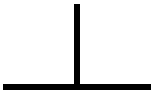
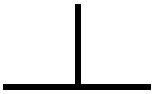
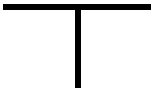
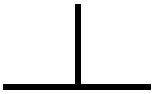
The standard process list is **std_dept.list**.

C I

How to interpret the spectrum

The appearances and features of signals for the multiplicity of resonance lines are shown.

Appearances of signals

θ	Multiplicity of resonance lines			
	>C< (Singlet)	−CH< (Doublet)	—CH_2— (Triplet)	−CH_3 (Quartet)
θ_1=45°				
θ_2=90°				
θ_3=135°				

Features

- The spectrum corresponding to each carbon group can be created from spectra θ_1 to θ_3.
- Signals of quaternary carbon and deuterated solvent do not appear.
- The sensitivity is almost the same as that of the INEPT method.
- Pulses can be repeated after the ^1H relaxation time (T_1).

C I

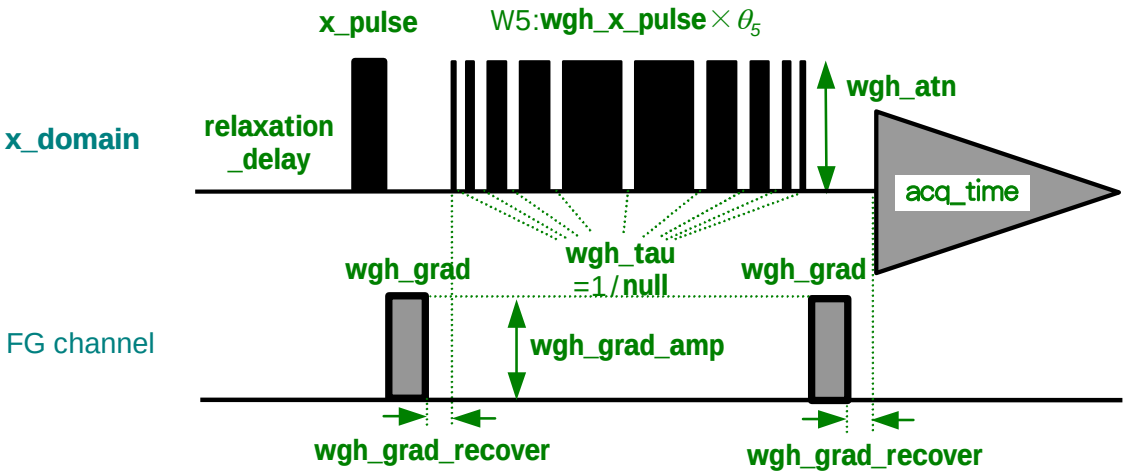
4.2.8 wgh.ex2

Measurement using the water gate pulse sequence for eliminating a solvent signal
Directory: **/usr/delta/global/experiments/1d**

Purpose

To reduce a signal that would overwhelm the desired signal, such as a water signal in an aqueous-solution sample.

Pulse sequences



W1: θ_1={90, 90}
W2: θ_2={45, 135, 45, 135}
W3: θ_3={20.8, 62.2, 131.6, 131.6, 62.2, 20.8}
W4: θ_4={10.4, 29.4, 60.5, 132.8, 132.8, 60.5, 29.4, 10.4}
W5: θ_5={7.8, 18.5, 37.2, 70, 134.2, 134.2, 70, 37.2, 18.5, 7.8}

Extension sequences

raw_suppression Select **Off, Raw** or **Rawscuba**. The default is **Off**.

dante_presat The default is **FALSE**.

irr_mode Select **Off, Presaturation**, or **Homo Decouple**. The default is **Off**.

tri_mode Select **Off, Presaturation**, or **Homo Decouple**. The default is **Off**.

Parameters

x_domain Observation nucleus. The default is **Proton**.

x_offset Observation center (peak to be eliminated). The default is **5 ppm**.

x_sweep Observation range. The default is **15 ppm**.

x_**points** Number of points to sample. The default is **4K**.

scans Number of scans to accumulate. The default is **16 times**.

x_prescans Number of dummy scans.

C I

x_pulse 90° pulse width **x90** set in the probe file.

x_atn Determines RF output. The default attenuator value is **xatn** set in the probe file. Every time 6 dB is added, the pulse width is halved.

watergate_selection
Select the water gate excitation characteristic. The default is **W5.**

wgh_x_pulse Pulse width of water gate. The default is the 90° pulse width **x90** set in the probe file.

wgh_null Water gate excitation range. The default is 5000 Hz.

wgh_tau Indicates the water gate pulse interval.

wgh_grad Pulse width of the PFG pulse. The default is **1 ms**.

wgh_grad_amp Output of the PFG pulse. The default is **20%.**

wgh_grad_shape Waveform of the PFG pulse. The default is **SQUARE**.

wgh_grad_recover
Recovery time after the PFG pulse. The default is **0.1 ms**.

relaxation_delay Waiting time between repeated pulses. The default is **3 s**.

repetition_time **relaxation_delay+ x_acq_time**.

Data processing

The standard process list is **std_proton.list**.

Supplementary note

Due to the water gate excitation characteristic, the bigger the number, the better the selectivity. However, the measurement is easily influenced by relaxation time.

C I

4.2.9 difference_noe_1d.ex2

1D NOE measurement by difference spectroscopy.
Directory**: /usr/delta/global/experiments/1d_noe**

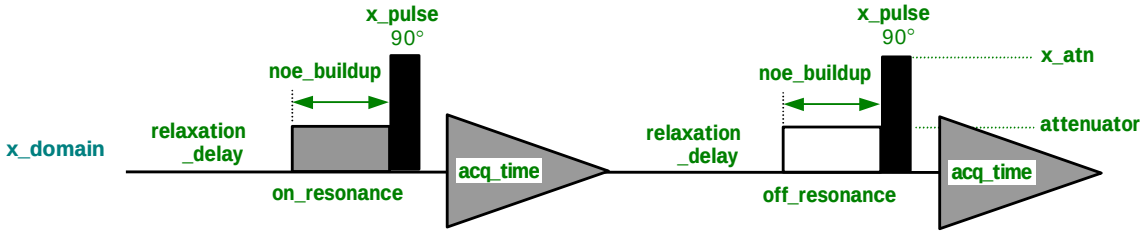
NOE is the abbreviation of Nuclear Overhauser Effect.

Purpose

To observe only the NOE signal of a specific peak by taking the difference between the same peaks before and after a specific peak is irradiated.

In this method, three-dimensional positional relationships among atomic groups can be obtained.

Pulse sequences



Extension sequences

dante_presat	The default is **FALSE**.
irr_mode	Select **Off, Presaturation** ,or **Homo Decouple**. The default is **Off**.
tri_mode	Select **Off, Presaturation** ,or **Homo Decouple**. The default is **Off**.

Parameters

x_domain	Observation nucleus. The default is **Proton**.
x_offset	Observation center. The default is **5 ppm**.
x_sweep	Observation range. The default is **15 ppm**.
x_points	Number of points to sample. The default is **16K**.
scans	Number of measurement (a multiple of eight). The default is **16** scans.
x_prescans	Number of dummy scans.
x_pulse	90° pulse width of the observation channel (^{1}H). The default is **x90** set in the probe file.
x_atn	Attenuator value **xatn** set in the probe file. Every time 6dB is added, the pulse width is halved.
on_resonance	Position (ppm) of the peak to be selectively irradiated. The default is 0 ppm.
off_resonance	Position (ppm) of the reference spectrum to be irradiated; sufficiently apart from that of the sample signal. The default is **–10** ppm.

C I

noe_buildup	Selective irradiation time. The default is **5 s.**
attenuator	Determines RF output for the selective irradiation pulse. The default is **40** dB. Every time 3 dB is added, the RF output is halved.
relaxation_delay	Waiting time between repeated pulses.
repetition_time	**relaxation_delay+ x_acq_time**.

Data processing

The standard process list is **std_proton.list.**

How to interpret the spectrum

Only NOE due to selective-excitation for a specific peak can be observed. Thus the spectrum gives information on three-dimensional positional relationships among atomic groups in the molecule.

C I

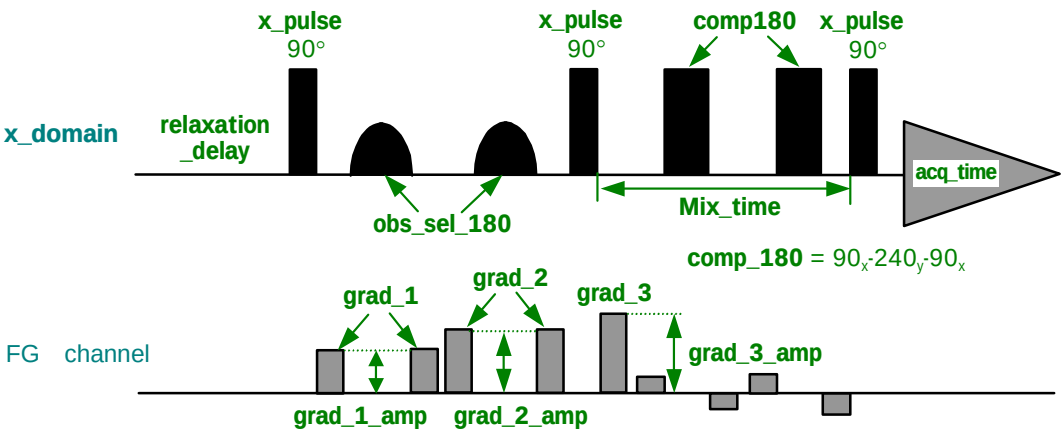
4.2.10 noe_1d_dpfgse.ex2

DPFG 1D NOE measurement using a shaped pulse
Directory: **/usr/delta/global/experiments/1d_noe**

Purpose

To observe only the NOE signal caused by selectively exciting a specific peak. This measurement provides information on three-dimensional positional relationships among atomic groups in the molecule.

Pulse sequences



Extension sequences

dante_presat	The default is **FALSE**.
irr_mode	Select **Off, Presaturation**, or **Homo Decouple**. The default is **Off.**
tri_mode	Select **Off, Presaturation**, or **Homo Decouple**. The default is **Off**.

Parameters

x_domain	Observation nucleus. The default is **Proton**.
x_offset	Observation center. The default is **5 ppm**.
x_sweep	Observation range. The default is **15 ppm**.
x_points	Number of points to sample. The default is **16K**.
scans	Number of scans to accumulate (a multiple of 16). The default is **16** scans.
x_prescans	Number of dummy scans.
x_pulse	90° pulse width of the observation channel (^{1}H). The default is **x90** set in the probe file.
x_atn	Attenuator value **xatn** set in the probe file. Every time 6 dB is added, the pulse width is halved.

C I

obs_sel_180	180° pulse width of the selective-excitation pulse. The default is twice the pulse width **x90_soft** set in the probe file.
obs _sel_atn	Determines RF output for the selective-excitation pulse. The default is the attenuator value **xatn_soft** set in the probe file. Every time 6 dB is added, the pulse width is halved.
obs_sel_offset	Resonance position of selective excitation. The default is the same as **x_offset**.
obs_sel _shape	Select the waveform of the selective-excitation pulse. The default is **GAUSS.**
mix_time	Mixing time. The default is **500 ms**.
relaxation_delay	Waiting time between repeated pulses. The default is **7 s**.
repetition_time	**relaxation_delay+ x_acq_time**.
grad_1	Pulse width of the first FG pulse (PFG1). The default is **1 ms**.
grad_1_amp	Pulse output of the first FG pulse (PFG1). The default is **20%**.
grad_2_amp	Pulse output of the second FG pulse (PFG2). The default is **30%**.
grad_3	Pulse width of the third FG pulse (PFG3). The default is **1 ms**.
grad_3_amp	Pulse output of the third FG pulse (PFG3). The default is **10%**.
grad_shape	Select the waveform of the FG pulse from **SQUARE, SINE**, and **GAUSS.** The default is **SINE**.
grad_recover	Recovery time after the FG pulse. The default is **0.1 ms**.

Data processing

The standard process list is **std_proton.list**.

How to interpret the spectrum

Only the peak changed by NOE due to selective excitation can be observed. Thus the spectrum gives information on three-dimensional positional relationships among atomic groups in the molecule.

C I

4.2.11 roesy_1d_dpfgse.ex2

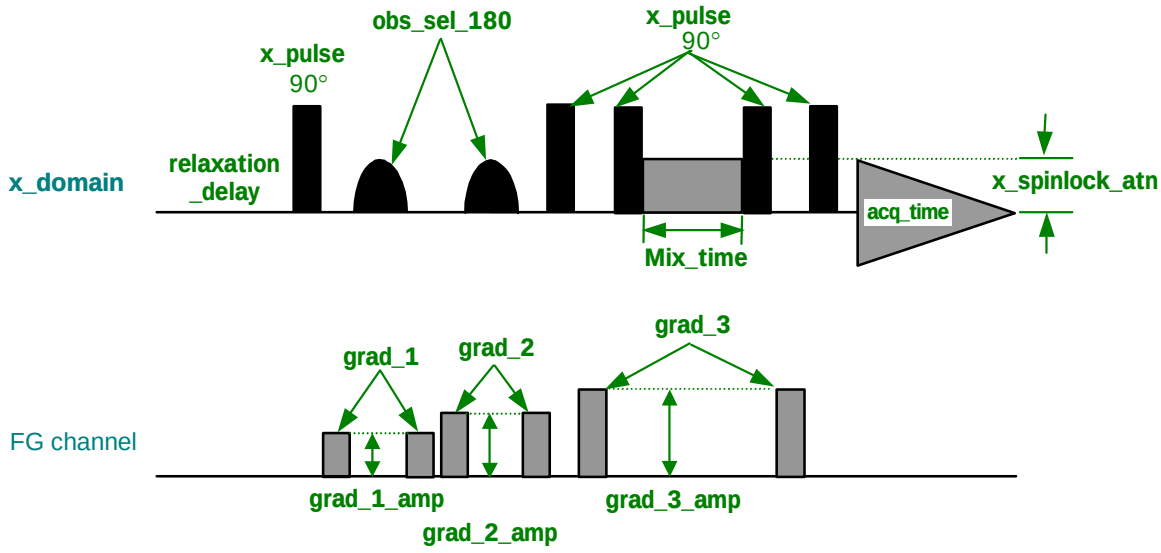
DPFG 1D ROESY measurement using shaped pulses
Directory: **/usr/delta/global/experiments/1d_roesy**

ROESY is the abbreviation of Rotating frame nuclear Overhauser Effect SpectroscopY.
ROESY is sometimes called CAMELSPIN. CAMELSPIN is the abbreviation of Cross relaxation Appropriate for Minimolecules Emulated by Locked Spins.

Purpose

To observe only the peaks enhanced by ROE (NOE in the rotating frame) due to selective excitation of a specific peak. This method is effective for samples having medium molecular weights of 1000 to 5000, whose NOE is difficult to observe.

Pulse sequences



Extension sequences

dante_presat	The default is **FALSE**.
irr_mode	Select **Off, Presaturation**, or **Homo Decouple**. The default is **Off**.
tri_mode	Select **Off, Presaturation**, or **Homo Decouple**. The default is **Off**.

Parameters

x_domain	Observation nucleus. The default is **Proton**.
x_offset	Observation center. The default is **5 ppm**.
x_sweep	Observation range. The default is **15 ppm**.
x_points	Number of points to sample. The default is **16K**.
scans	Number of scans to accumulate (a multiple of 16). The default is **16** scans.

C I

x_prescans	Number of dummy scans.
x_pulse	90° pulse width of observation channel (^{1}H). The default is **x90** set in the probe file.
x_atn	The attenuator value is **xatn** set in the probe file. Every time 6 dB is added, the pulse width is halved.
obs_sel_180	Set 180° pulse width of the selective-excitation pulse. The default value is twice the pulse width **x90_soft**×2 which is set in the probe file.
obs_sel_atn	Set RF output amplitude of the selective-excitation pulse. The default is the attenuator value **xatn_soft** which is set in the probe file.
obs_sel_offset	Resonance position of the peak to be selectively excited. The default is the same as **x_offset**.
obs_sel _shape	Waveform of the selective-excitation pulse. The default is **GAUSS**.
x_spinlock_mode	Select the mode of the spin lock pulse. The default is **18 dB down**.
x_spinlock_atn	Determines RF output for the spin lock pulse. The default is **x_atn** minus the value selected in **x_spinlock_mode.**
spinlock_strength	Indicates the frequency range to be excited by the spin lock pulse.
mix_time	Mixing time. The default is **250 ms**.
relaxation_delay	Waiting time between repeated pulses. The default is **7 s**.
repetition_time	**relaxation_delay+ x_acq_time**.
grad_1	Pulse width of the 1st FG pulse (PFG1). The default is **1 ms**.
grad_1_amp	Pulse output of the 1st FG pulse (PFG1). The default is **20%.**
grad_2	Pulse width of the 2nd FG pulse (PFG2). The default is the same as **grad_1**.
grad_2_amp	Pulse output of the 2nd FG pulse (PFG2). The default is **30%**.
grad_3_amp	Pulse output of the 3rd FG pulse (PFG3). The default is **5%.**
grad_shape	Waveform of the FG pulse. Select **SQUARE**, **SINE**, or **GAUSS.** The default is **SINE**.
grad_recover	Recovery time after the FG pulse. The default is **0.1 ms**.

Data processing

The standard process list is **std_proton.list**.

How to interpret the spectrum

Only the ROE (NOE in the rotating frame) signal caused by selectively exciting a specific peak can be observed. This method is effective for samples having medium molecular weights of 1000 to 5000, whose NOE is difficult to observe.

Supplementary note

- Check the accurate value of the selective-excitation pulse **obs_sel_180** using **single_shaped_pulse.ex2.**
- About the intensity of spin lock
  In this measurement method, the spin lock intensity is adjusted by the set attenuator value from the output at full power.
  The 90° pulse width during the spin-locked period is given by

$$c = a \times \sqrt{\frac{1}{10^{(0.1 \times b)}}}$$

  where a (s): 90° pulse width at full power
  b (dB): Attenuator value which was set from this c

  The spin lock intensity is computed as

$$\text{Spin lock intensity} = \frac{1}{4 \times c}$$

  Set the spin lock intensity equal to the observation range.
- It is recommended that you stop spinning of the sample tube before measurement.

C I

4.2.12 tocsy_1d_dpfgse.ex2

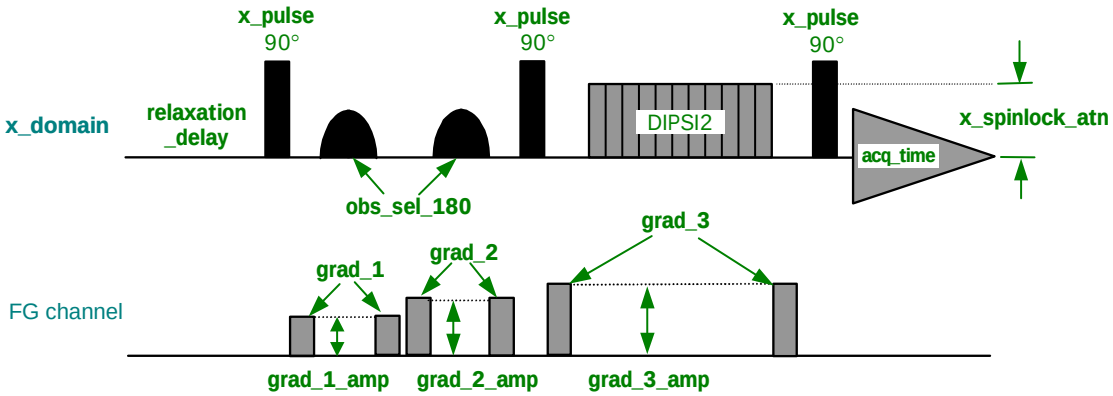
DPFG 1D TOCSY measurement using a shaped pulse.
Directory: /usr/delta/global/experiments/1d_tocsy

TOCSY is the abbreviation of TOtal Correlation SpectroscopY.
TOCSY is sometimes called HOHAHA. HOHAHA is the abbreviation of HOmo nuclear HArtmann-HAhn spectroscopy.

Purpose

To observe the connection of spin coupled peaks while a specific peak is selectively excited. This measurement clarifies the spin-coupling network including the selective peak.

Pulse sequence



Extension sequences

dante_presat The default is **FALSE**.

irr_mode Select **Off, Presaturation**, or **Homo Decouple**. The default is **Off**.

tri_mode Select **Off, Presaturation**, or **Homo Decouple**. The default is **Off.**

Parameters

x_domain Observation nucleus. The default is **Proton**.

x_offset Observation center. The default is **5 ppm**.

x_sweep Observation range. The default **is 15 ppm.**

x_points Number of points to sample. The default is **16K**.

scans Number of scans to accumulate (a multiple of 16). The default is **16** scans.

x_prescans Number of dummy scans.

x_pulse 90° pulse width of the observation channel (^{1}H). The default is **x90** set in the probe file.

C I

x_atn	Determines RF output; the attenuator value **xatn** set in the probe file. Every time 6 dB is added, the pulse width is halved.
obs_sel_180	180° pulse width of the selective-excitation pulse. The default is twice the pulse width **x90_soft** set in the probe file.
obs_sel_atn	Determines RF output for the selective-excitation pulse. The default is the attenuator value **xatn_soft** set in the probe file. Every time 6 dB is added, the pulse width is halved.
obs_sel_offset	Resonance position of the peak to be selectively excited. The default is the same as **x_offset**.
obs_sel _shape	Waveform of the selective-excitation pulse. The default is **GAUSS**.
x_spinlock_pulse	90° pulse width of the spin lock pulse. The default is **x90_ spin** set in the probe file.
x_spinlock_atn	Determines RF output for the spin lock pulse. The default is **xatn_spin** set in the probe file.
delta	Waiting time.
mix_time	Mixing time. The default is **50 ms**.
relaxation_delay	Waiting time between repeated pulses. The default is **7 s**.
repetition_time	**relaxation_delay+ x_acq_time**.
mix_time_loop	Number of irradiation times of the spin lock pulse.
total_mix_time	Total mixing time.
grad_1	Pulse width of the 1st FG pulse (PFG1). The default is **1 ms**.
grad_1_amp	Pulse output of the 1st FG pulse (PFG1). The default is **20%.**
grad_2	Pulse width of the 2nd FG pulse (PFG2). The default is the same as **grad_1**.
grad_2_amp	Pulse output of the 2nd FG pulse (PFG2). The default is **30%.**
grad_3	Pulse width of 3rd FG pulse (PFG3). The default is the same **grad_1.**
grad_3_amp	Pulse output of the 3rd FG pulse (PFG3). The default is **5%.**
grad_shape	Waveform of the FG pulse. Select **SQUARE**, **SINE**, or **GAUSS**. The default is **SINE**.
grad_recover	Recovery time after the FG pulse. The default is **0.1 ms**.

Data processing

The standard process list is **std_proton.list.**

How to interpret the spectrum

A specific peak is selectively excited, and then spin-spin coupling to its excited peak can be observed. The spin-coupling network including the selectively excited peak can be clarified.

C I

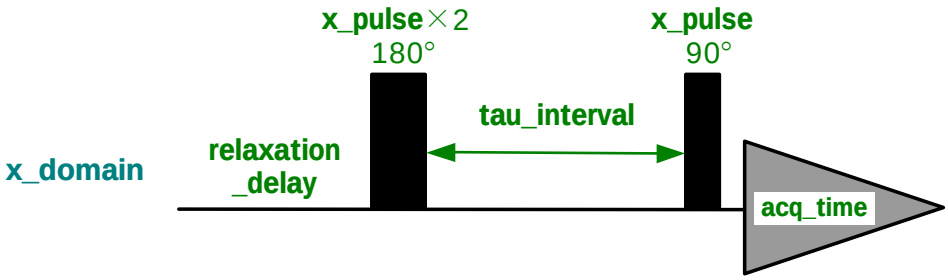
4.2.13 double_pulse.ex2

Measurement using double pulses
Directory: /usr/delta/global/experiments/relaxation

Purpose

To evaluate T_1 (the longitudinal relaxation time) simply.

Pulse sequence



Extension sequences

dante_presat	The default is **FALSE**.
irr_mode	Select **Off, Presaturation**, or **Homo Decouple**. The default is **Off**.
tri_mode	Select **Off, Presaturation**, or **Homo Decouple**. The default is **Off.**

Parameters

x_domain	Observation nucleus. The default is **Proton**.
x_offset	Observation center. The default is **5 ppm**.
x_sweep	Observation range. The default is **15 ppm**.
x_points	Number of points to sample. The default is **16K**.
scans	Number of scans to accumulate (a multiple of 8). The default is **eight** scans.
x_prescans	Number of dummy scans.
x_pulse	Number of preliminary scans before accumulation pulse width of observation channel (^{1}H).The default is **x90** set in the probe file.
x_atn	Determines RF output; the attenuator value **xatn** set in the probe file. Every time 6 dB is added, the pulse width is halved.
tau_interval	Interval between two pulses (delay time for the relaxation). The default is **10 s**.
relaxation_delay	Waiting time between repeated pulse sequences. The default is **7 s**.
repetition_time	**relaxation_delay+ x_acq_time**.

Data processing

The standard process list is **std_proton.list.**

How to interpret the spectrum

In the case of single exponential decay, the observed magnetization M(τ) at the pulse interval τ is expressed by the following equation.

$$M(\tau) = M_0(1 - 2\exp\left(\frac{-\tau}{T_1}\right))$$

When the magnetization M(τ) become zero, the tau value (τ) is called the null point. If the null point is indicated by τ_{null}, T_1 is given by the following equation.

$$T_1 = \frac{\tau_{null}}{\ln 2} = 1.44 \times \tau_{null}$$

C I

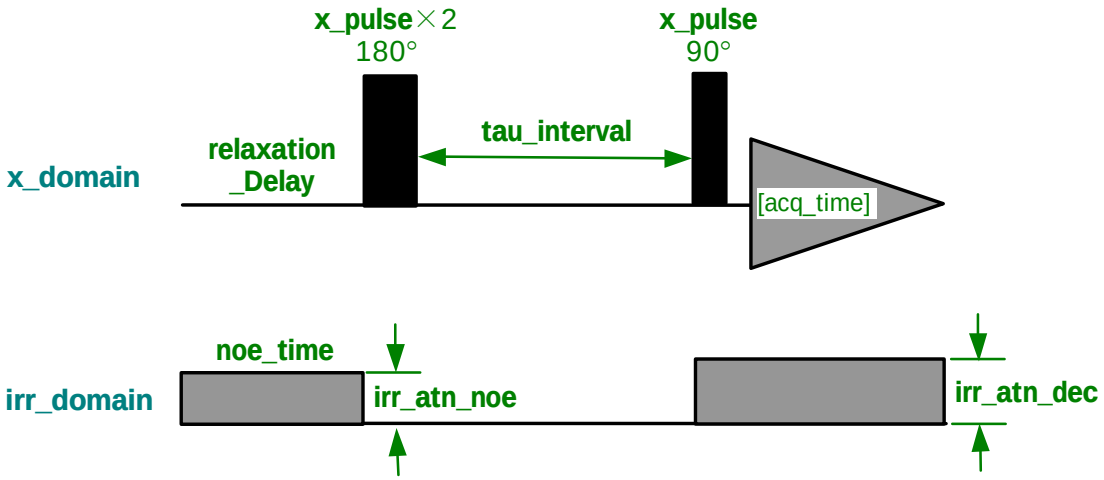
4.2.14 double_pulse_dec.ex2

Measurement using double pulses with heteronuclear decoupling
Directory: /usr/delta/global/experiments/relaxation

Purpose

To evaluate T_1 (the longitudinal relaxation time) simply with heteronucleus decoupling.

Pulse sequences



Extension sequences

noe	The default is **TRUE**.
decoupling	The default is **TRUE**.

Parameters

x_domain	Observation nucleus. The default is **Carbon13**.
x_offset	Observation center. The default is **100 ppm**.
x_sweep	Observation range. The default is **250 ppm**.
x_points	Number of points to sample. The default is **32K**.
scans	Number of scans to accumulate (a multiple of 8). The default is eight scans.
x_prescans	Number of dummy scans.
x_pulse	90° pulse width of the observation channel (^{13}C). The default is **x90** set in the probe file.
x_atn	Determines RF output. The default is **xatn** set in the probe file. Every time 6 dB is added, the pulse width is halved.
tau_interval	Interval between two pulses (delay time for the relaxation). The default is **10 s**.

C I

relaxation_delay Waiting time between repeated pulse sequences. The default is **7 s**.

repetition_time **relaxation_delay + x_acq_time**.

Data processing

The standard process list is **std_carbon.list**.

How to interpret the spectrum

In the case of single exponential decay, the observed magnetization M(τ) at the pulse interval τ is expressed by the following equation.

$$M(\tau) = M_0(1 - 2\exp\left(\frac{-\tau}{T_1}\right))$$

When the magnetization M(τ) become zero, the tau value (τ) is called the null point. If the null point is indicated by τ_{null}, T_1 is given by the following equation.

$$T_1 = \frac{\tau_{null}}{\ln 2} = 1.44 \times \tau_{null}$$

C I

4.3 2D MEASUREMENT

4.3.1 cosy_pfg.ex2

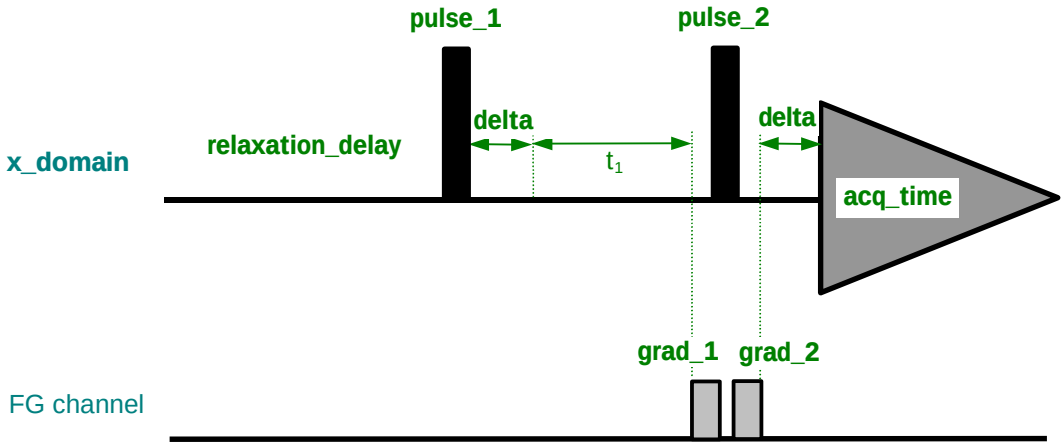
PFG homonuclear shift correlation measurement
Directory: /usr/delta/global/experiments/cosy

PFG is the abbreviation of Pulsed Field Gradient.
COSY is the abbreviation of COrrelation SpectroscopY.

Purpose

To observe correlation signals between directly J-coupled peaks. This measurement gives information on connections of spin-spin interaction between the ^{1}H peaks. The use of PFG results in a 2D spectrum with one scan.

Pulse sequences



Extension sequences

dante_presat	The default is **FALSE**.
irr_mode	Select **Off, Presaturation**, or **Homo decouple**. The default is **Off.**
tri_mode	Select **Off, Presaturation**, or **Homo Decouple.** The default is **Off.**

Parameter

x_domain	Observation nucleus. The default is **Proton**.
x_offset	Observation center. The default is **5 ppm**.
x_sweep	Observation range. The default is **15 ppm**.
x_points	Number of points to sample along the t_2 axis. The default is **1024**.
scans	Number of scans to accumulate. The default is **1** scan.
x_prescans	Number of dummy scans. The default is four scans.
y_points	Number of points to sample along the t_1 axis. The default is 256.
x_90_width	90° pulse width set in the probe file.

C I

x_atn	**A**ttenuator value **x_atn** set in the probe file.
pulse_angle _1	Flip angle of the first pulse. The default is **90 deg**.
pulse_1	First pulse width. It is computed as $$\mathbf{x\_90\_width} \times \frac{\mathbf{pulse\_angle\_1}}{90^\circ}$$
pulse_angle _2	Flip angle of the second pulse. The default is **90 deg**.
pulse_2	Pulse width of the second pulse. It is computed as $$\mathbf{x\_90\_width} \times \frac{\mathbf{pulse\_angle\_2}}{90^\circ}$$
delta	Waiting time for long-range J coupling measurement. The default is **0 ms**.
relaxation_delay	Waiting time between repeated pulse sequences. The default is **1.5 s**.
repetition_time	**relaxation_delay+ x_acq_time.**
grad_1	Pulse width of the first FG pulse (**PFG1**). The default is **1 ms**.
grad_1_amp	Pulse output of the first FG pulse (**PFG1**). The default is **5%.**
grad_2	Pulse width of the second FG pulse (**PFG2**). The default is the same as **grad_1**.
grad_2_amp	Pulse output of the second FG pulse **(PFG2**). The default is the same as **grad_1_amp.**
grad_shape_type	Waveform of the FG pulse. Select **GAUSS, SINE,** or **SQUARE**. The default is **SINE**.
grad_recover	Recovery time after the FG pulse. The default is **0.1 ms**.

Data processing

The standard process list is **std_cosy_abs.list.**

How to interpret the spectrum

Both the f_2 axis and the f_1 axis represent ^{1}H chemical shift. The correlation signal appears at the points where the perpendicular lines drawn at the peak positions on the f_2 axis and the f_1 axis cross.

Supplementary note

- Setting the second pulse width **pulse_2** to a 45° pulse makes it easy to observe correlation signals near the diagonal signal. This measurement also gives information on the relative sign of J coupling.
- Set the parameters as follows:
  PFG1 (**grad_1** × **grad_1_amp**) : PFG2 (**grad_2** × **grad_2_amp**) = 1 : 1.

C I

4.3.2 dqf_cosy_phase.ex2

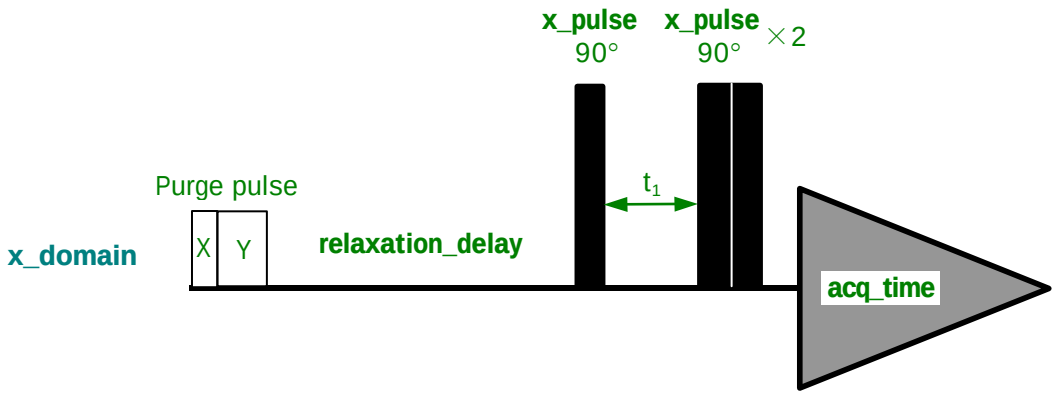
Phase-sensitive double quantum filtered COSY measurement
Directory: /usr/delta/global/experiments/dqf_cosy

✍ COSY is the abbreviation of COrrelation SpectroscopY.

Purpose

To observe correlation signals between J-coupled peaks.
Using the double quantum filter, signals having no J-coupling with ^{1}H (singlet signals such as solvent or isolated –CH_3 group) are eliminated. The method is appropriate for observing correlation signals located near the diagonal signals.

Pulse sequence



Extension sequences

dante_presat	The default is **FALSE**.
irr_mode	Select **Off, Presaturation**, or **Homo Decouple.** The default is **Off**.
tri_mode	Select **Off, Presaturation**, or **Homo Decouple.** The default is **Off**.

Parameters

x_domain	Observation nucleus. The default is **Proton**.
x_offset	Observation center. The default is **5 ppm**.
x_sweep	Observation range. The default is **15 ppm**.
x_points	Number of points to sample along the t_2 axis. The default is **1024**.
y_points	Number of points to sample along the t_1 axis. The default is **256**.
scans	Number of scans to accumulate. The default is **16** scans
x_prescans	Number of dummy scans. The default is four scans.
x_pulse	90° pulse width of the observation channel (^{1}H). The default is the **x90** value set in the probe file.
x_atn	Attenuator value **xatn** set in the probe file. Every time 6 dB is added, the pulse width is halved.

relaxation_delay Waiting time between repeated pulses. The default is **1.5 s**.

repetition_time **relaxation_delay+ x_acq_time**.

y_p1_correction Value to be entered in the first-order term (P1) for the phase correction of the t_1 axis.

Data processing

The standard process list is **2d_cosy_phase_autophase.list**.

How to interpret the spectrum

Both the f_2 axis and the f_1 axis represent ^1H chemical shift. The correlation signal appears at the points where the perpendicular lines drawn at the peak positions on the f_2 axis and the f_1 axis cross. The correlation signal does not appear at the points between signals having no J-coupling.

C I

4.3.3 hetcor.ex2

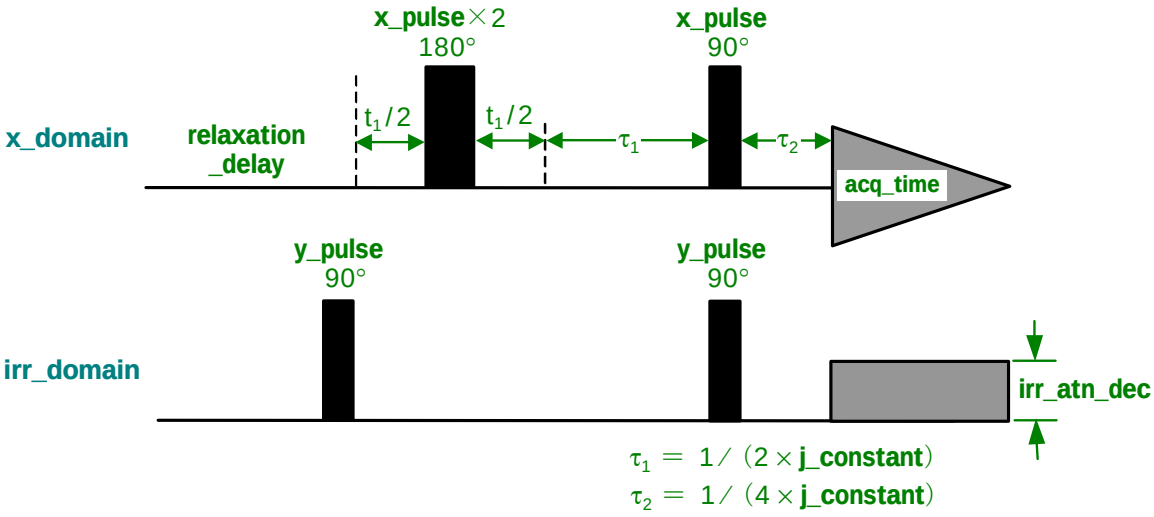
Heteronuclear shift correlation measurement
Directory : / usr/delta/global/experiments/hector

✍ HETCOR is the abbreviation of HETeronuclear CORrelation.

■ Purpose

To observe correlation signals between the directly J-coupled heteronuclear peaks.

■ Pulse sequences



■ Extension sequences

decoupling The default is **TRUE**.

■ Parameters

x_domain Observation nucleus. The default is **Carbon13.**

x_offset Observation center. The default is **100 ppm**.

x_sweep Observation range. The default is **250 ppm**.

x_points Number of points to sample along the t_2 axis. The default is **1024**.

scans Number of scans to accumulate (a multiple of eight). The default is eight scans.

x_prescans Number of dummy scans. The default is four scans.

y_domain Observation nucleus of the f_1 axis. The default is **Proton**.

y_offset Observation center of the f_1 axis. The default is 5 ppm.

y_sweep Observation range of the f_1 axis. The default is 15 ppm.

y_points Number of points to sample along the t_1 axis. The default is **128**.

C I

x_pulse	90° pulse width of the observation channel (^{13}C) on the f_2 axis. The default is **x90** in the probe file.
x_atn	Attenuator value **xatn** set in the probe file. Every time 6 dB is added, the pulse width is halved.
y_pulse	90° pulse width of the observation channel (^{1}H) on the f_1 axis. The default is **y90** set in the probe file.
y_atn	Attenuator value **yatn** set in the probe file. Every time 6 dB is added, the pulse width is halved.
j_constant	Value of $^{1}J_{CH}$. The default is **140 Hz**.
relaxation_delay	Waiting time between repeated pulse sequences. The default is **1.5 s**.

Data processing

The standard process list is 2**d_hetcor_abs.list**.

How to interpret the spectrum

The correlation signals appear at the points where the perpendicular lines drawn at the peak positions on the f_2 axis and the f_1 axis cross.

C I

4.3.4 coloc.ex2

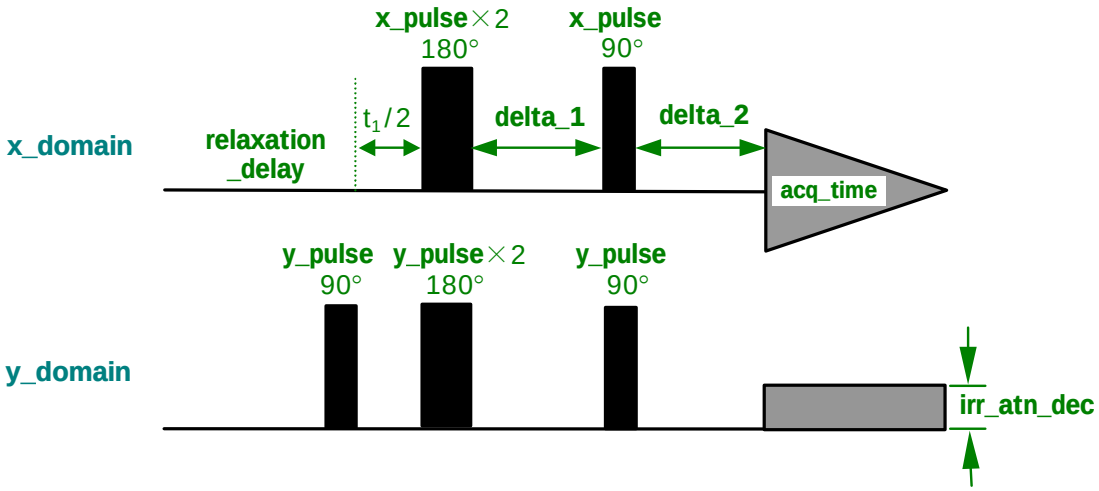
Heteronuclear long-range shift correlation measurement
Directory: /usr/delta/global/experiments/hetcor

COLOC is the abbreviation of COrrelation spectroscopy via LOng range Coupling.

Purpose

To observe correlation signals between peaks having long-range spin-spin coupling. This method is appropriate for the assignment of quaternary carbon.

Pulse sequences



Extension sequences

decoupling The default is **TRUE**.

Parameters

x_domain Observation nucleus. The default is **Carbon13**.

x_offset Observation center. The default is **100 ppm**.

x_sweep Observation range. The default is **250 ppm**.

x_points Number of points to sample along the t_2 axis. The default is **1024**.

scans Number of scans to accumulate (a multiple of eight). The default is **eight** scans.

x_prescans Number of dummy scans. The default is four scans.

y_domain Observation nucleus of the f_1 axis. The default is **Proton**.

y_offset Observation center of the f_1 axis. The default is **5 ppm**.

y_sweep Observation range of the f_1 axis. The default is **15 ppm**.

y_points Number of points to sample along the t_1 axis. The default is **128**.

C I

x_pulse	90° pulse width of the observation channel (^{13}C) of the f_2 axis. The default is **x90** in the probe file.
x_atn	Attenuator value **xatn** set in the probe file. Every time 6 dB is added, the pulse width is halved.
y_pulse	90° pulse width of the observation channel (^{1}H) on the f_1 axis. The default is **y90** in the probe file.
y_atn	Attenuator value **yatn** set in the probe file. Every time 6 dB is added, the pulse width is halved.
long_range_j	Value of the long range J_{CH}. The default is **10 Hz**.
delta_1	Waiting time. When y_points/ (2 × y_sweep) > 1/(2 × long_range_j), set **delta_1** to y_points/(2 × y_sweep). When y_points/ (2 × y_sweep) < 1/(2 × long_range_j), set **delta_1** to 1/(2 × long_range_j).
delta_2	Waiting time. 1/(3 × long_range_j)
max_y_points	Maximum value of **y_points**.
relaxation_delay	Waiting time between repeated pulses. The default is **1.5 s**.

Data processing

The standard process list is 2**d_hetcor_abs.list**.

How to interpret the spectrum

The long-range correlation signals appear at the points where the perpendicular lines drawn at the peak positions on the f_2 axis and the f_1 axis cross.

C I

4.3.5 hmbc_pfg.ex2

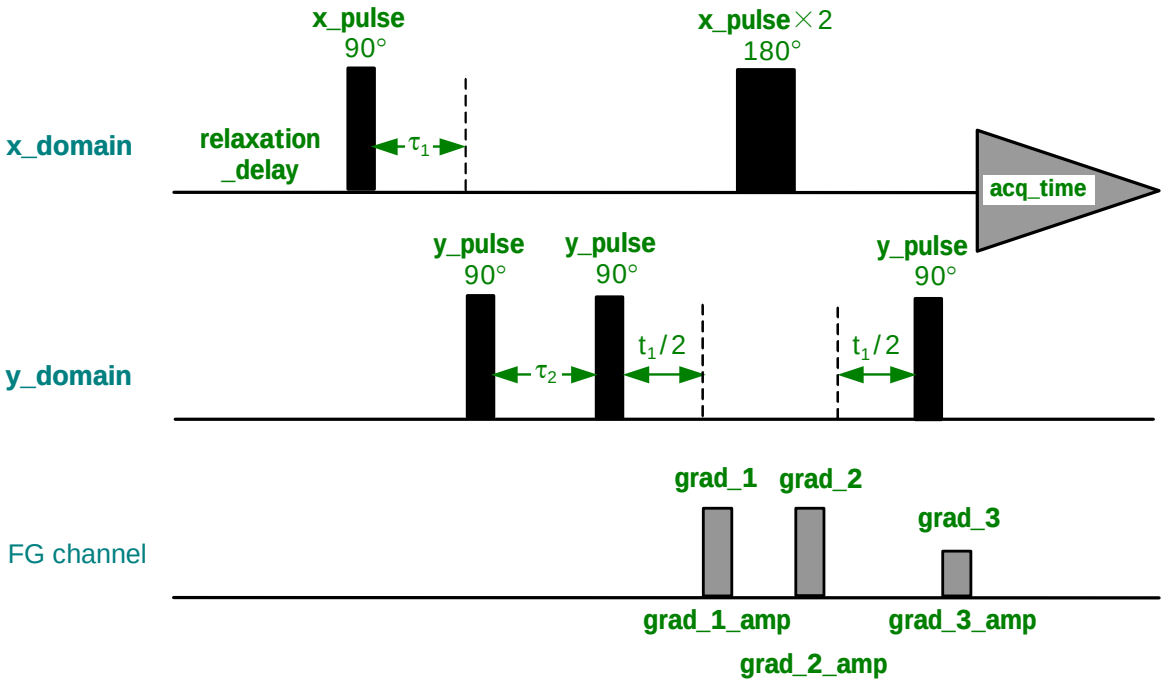
PFG ^{1}H observation heteronuclear long-range shift correlation HMBC measurement (absolute-value type)
Directory: **/usr/delta/global/experiments/hmbc**

PFG is the abbreviation of Pulsed Field Gradient.
HMBC is the abbreviation of Heteronuclear Multiple Bond Connectivity.

Purpose

To observe long-range correlation signals between ^{1}H and ^{13}C nuclei.
The correlation signals between quaternary carbons and ^{1}H nuclei can also be observed. By observing the ^{1}H nucleus, the S/N ratio is enhanced compared with that using the ^{13}C observation heteronuclear long-range shift correlation (**coloc.ex2**) method.

Pulse sequences



τ_1 = 1 / (2×**j_constant**)
τ_2 = 1 / (2×**long_range_j**) - 1 / (2×**j_constant**)

Extension sequences

dante_presat The default is FALSE.

tri_mode Select **Off**, **Presaturation**, or **Homo Decouple**. The default is **Off**.

Parameters

x_domain Observation nucleus of the f_2 axis. The default is **Proton**.

x_offset Observation center of the f_2 axis. The original value is **5 ppm**.

C I

x_sweep	Observation range of the f_2 axis. The default is **15 ppm**.
x_points	Number of points to sample along the t_2 axis. The default is **2048**.
scans	Number of scans to accumulate (a multiple of four). The default is **4** scans.
x_prescans	Number of dummy scans. The default is four scans.
y_domain	Observation nucleus of the f_1 axis. The default is **Carbon13**.
y_offset	Observation center of the f_1 axis. The default is **100 ppm**.
y_sweep	Observation range of the f_1 axis. The default is **250 ppm**.
y_points	Number of points to sample along the t_1 axis. The default is **256**.
x_pulse	90° pulse width of the observation channel (^{1}H) of the f_2 axis. The default is **x90** in the probe file.
x_atn	Attenuator value **xatn** set in the probe file. Every time 6 dB is added, the pulse width is halved.
y_pulse	90° pulse width of the observation channel (^{13}C) of the f_1 axis. The default is **y90** in the probe file.
y_atn	Attenuator value **yatn** set in the probe file. Every time 6 dB is added, the pulse width is halved.
j_constant	Value of $^{1}J_{CH}$. The default is **140 Hz**.
long_range_j	Value of the long range J_{CH}. The default is **8 Hz**.
relaxation_delay	Waiting time between repeated pulses. The default is **1.5 s**.
repetition_time	**relaxation_delay+ x_acq_time.**
grad_selection	Relative intensity ratio of the PFG applied to **y_domain**.
grad_1	Pulse width of the first FG pulse (PFG1). The default is **1 ms**.
grad_1_amp	Pulse output of the first FG pulse (PFG1). The default is **60 %.**
grad_2	Pulse width of the second FG pulse (PFG2). The default is the same as **grad_1**.
grad_2_amp	Pulse output of the second FG pulse (PFG2). The default is the same as **grad_1_amp**.
grad_3	Pulse width of the third FG pulse (PFG3). The default is the same as **grad_1.**
grad_3_amp	Pulse output of the third FG pulse (PFG3). The default is computed from **grad_1** and the intensity ratio of the PFG to be applied to **y_domain.**
grad_shape	Waveform of the FG pulse. SELECT **SQUARE, SINE**, or **GAUSS**. The default is **SINE**.
grad_recover	Recovery time after the FG pulse. The default is **0.1 ms**.

C I

Data processing

The standard process list is **2d_hmbc_abs.list**.

How to interpret the spectrum

The f_2 axis represents the ^{1}H chemical shift and the f_1 axis is the ^{13}C chemical shift. The correlation signals due to the long-range coupling between ^{1}H and ^{13}C appear at the points where the perpendicular lines drawn at the peak positions on the f_2 axis and the f_1 axis cross. The correlation signals of the direct coupling between the ^{13}C and ^{1}H are also observed. However, these signals can be distinguished, as the latter signals are split due to $^{1}J_{CH}$ along the f_2 axis.

Supplementary note

- The ratios of the gradient pulses are as follows:
  For the ^{13}C nucleus, PFG1 : PFG2 : PFG3 = 2 : 2 : 1.
  For the ^{15}N nucleus, PFG1 : PFG2 : PFG3 = 4.94 : 4.94 : 1.
  For the ^{29}Si nucleus, PFG1 : PFG2 : PFG3 = 2.52 : 2.52 : 1.
  For the ^{31}P nucleus, PFG1 : PFG2 : PFG3 = 1.24 : 1.24 : 1.
  Here, PFG1 = **grad_1** × **grad_1_amp**, PFG2 = **grad_2** × **grad_2_amp**,
  PFG3 = **grad_3** × **grad_3_amp**.
- The standard value of **long_range_j** is **8 Hz** for ^{13}C and ^{15}N.
  Be careful in that the value of **long_range_j** depends on the sample.
- If you set **scans** to an odd number, insert **dc_balance** at the top of the process list of the X axis (the f_2 axis).
- It is recommended that you stop spinning the sample tube during measurement.

C I

4.3.6 hmqc_pfg.ex2

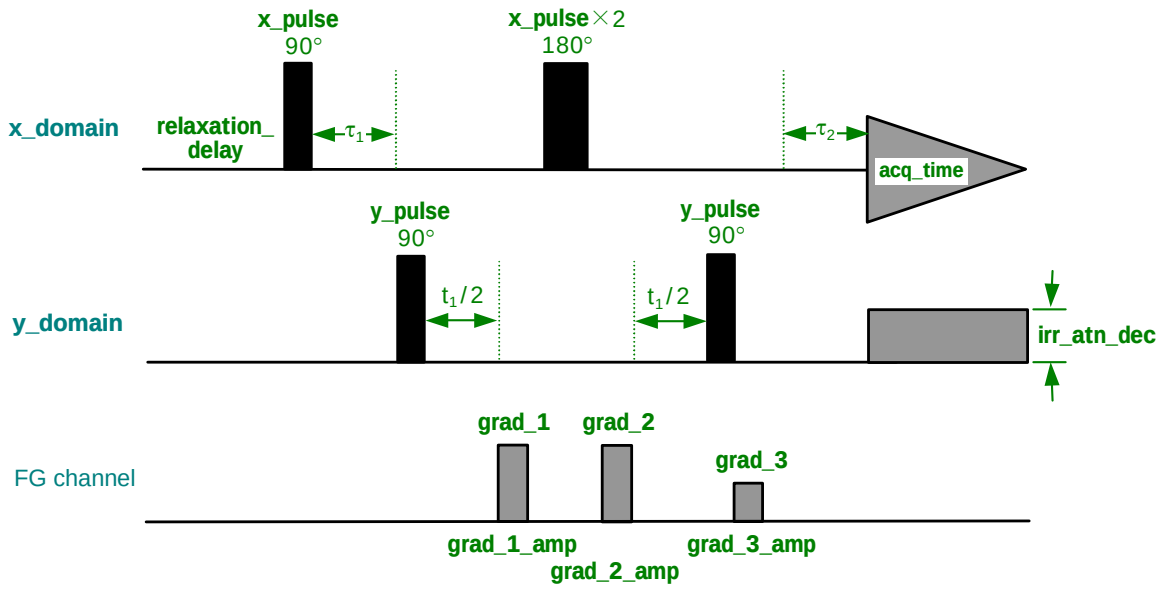
PFG ^{1}H observation heteronuclear shift correlation HMQC measurement
Directory: /usr/delta/global/experiments/hmqc

PFG is the abbreviation of Pulsed Field Gradient.
HMQC is the abbreviation of Heteronuclear Multi Quantum Coherence.

Purpose

To observe correlation signals between directly coupled ^{1}H and ^{13}C.
Since ^{1}H is observed, this measurement enhances the S/N ratio, compared with ^{13}C observation heteronuclear shift correlation measurement.

Pulse sequences



$\tau_1 = 1/(2 \times$ **j_constant**$)$
$\tau_2 = 1/(2 \times$ **j_constant**$) -$ **grad_3**

Extension sequences

decoupling	The default is **TRUE**.
presat_timing	The default is the same as **relaxation_delay**.
dante_presat	The default is **FALSE**.
tri_mode	Select **Off, Presaturation**, or **Homo Decouple**. The default is **Off**.

Parameters

x_domain	Observation nucleus of the f_2 axis. The default is **Proton**.
x_offset	Observation center of the f_2 axis. The default is **5 ppm**.
x_sweep	Observation range of the f_2 axis. The default is **15 ppm**.
x_points	Number of points to sample along the t_2 axis. The default is **1024**.

C I

scans	Number of scans to accumulate. The default is **1** scans.
x_prescans	Number of dummy scans. The default is four scans.
y_domain	Observation nucleus of the f_1 axis. The default is **Carbon13**.
y_offset	Observation center of the f_1 axis. The default is **85 ppm**.
y_sweep	Observation range of the f_1 axis. The default is **170 ppm**.
y_points	Number of points to sample along the t_1 axis. The default is **256**.
x_pulse	90° pulse width of the observation channel (^{1}H) of the f_2 axis. The default is **x90** in the probe file.
x_atn	Attenuator value **xatn** set in the probe file. Every time 6 dB is added, the pulse width is halved.
y_pulse	90° pulse width of the observation channel (^{13}C) of the f_1 axis. The default is **y90** set in the probe file.
y_atn	Attenuator value **yatn** set in the probe file. Every time 6 dB is added, the pulse width is halved.
j_constant	Value of $^1J_{CH}$. The default is **140 Hz**.
relaxation_delay	Waiting time between repeated pulse sequences. The default is **1.5 s**.
repetition_time	**relaxation_delay+ x_acq_time**.
grad_selection	Relative intensity ratio of the PFG to be applied to **y_domain.**
grad_1	Pulse width of the first FG pulse (PFG1). The default is **1 ms**.
grad_1_amp	Pulse output of the first FG pulse (PFG1). The default is **60%.**
grad_2	Pulse width of the second FG pulse (PFG2).The default is the same as **grad_1.**
grad_2_amp	**P**ulse output of the second FG pulse (PFG2).The default is the same as **grad_1_amp**.
grad_3	Pulse width of the third FG pulse (**PFG3**).The default is the same as **grad_1.**
grad_3_amp	Pulse output of the third FG pulse (**PFG**3).The default is computed from **grad_1** and the intensity ratio of the PFG to be applied to **y_domain.**
grad_shape	Waveform of the FG pulse. Select **SQUARE, SINE**, or **GAUSS**. The default is **SINE**.
grad_recover	Recovery time after the FG pulse. The default is **0.1 ms**.

Data processing

The standard process list is **2d_inverse_abs.list.**

How to interpret the spectrum

The f_2 axis represents the ^{1}H chemical shift and the f_1 axis is the ^{13}C chemical shift. The correlation signals between ^{1}H and ^{13}C appear at the points where the perpendicular lines drawn at the peak positions on the f_2 axis and the f_1 axis cross. The correlation signals indicate that the corresponding ^{1}H and ^{13}C are directly coupled.

Supplementary note

- The ratio of the gradient pulse is as follows.
  For the ^{13}C nucleus, PFG1 : PFG2 : PFG3 = 2 : 2 : 1.
  For the ^{15}N nucleus, PFG1 : PFG2 : PFG3 = 4.94 : 4.94 : 1.
  For the ^{29}Si nucleus, PFG1 : PFG2 : PFG3 = 2.52 : 2.52 : 1.
  For the ^{31}P nucleus, PFG1 : PFG2 : PFG3 = 1.24 : 1.24 : 1.
  Here, PFG1 = **grad_1** × **grad_1_amp**, PFG2 = **grad_2** × **grad_2_amp**, PFG3 = **grad_3** × **grad_3_amp**.
- Set J_{XH} as follows.
  J_{CH} = 100 to 250 Hz (standard: 145 Hz)
  J_{NH} = 60 to 140 Hz (standard: 95 Hz)
  J_{SiH} = 140 to 500 Hz
  J_{PH} = 37 to 1100 Hz
- If you set **scans** to an odd number, insert **dc_balance** at the top of the process list of the X axis (the f_2 axis).
- It is recommended that you stop spinning the sample tube during measurement.

C I

4.3.7 hsqc_dec_phase_pfgzz.ex2

Phase-sensitive HSQC measurement
Directory: /usr/delta/global/experiments/hsqc

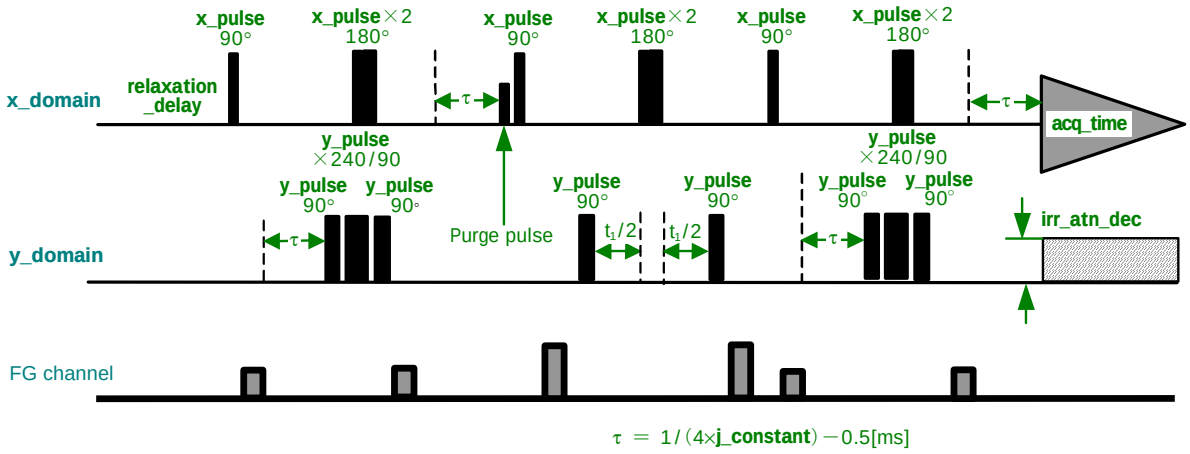
HSQC is the abbreviation of Heteronuclear Single Quantum Coherence.

Purpose

To observe correlation signals between ^{1}H and ^{13}C which are directly coupled.

Since ^{1}H is observed, this measurement enhances the S/N ratio, compared with ^{13}C observation heteronuclear shift correlation measurement. Selecting single quantum coherence, in principle, makes the resolution in the f_1 axis better than HMQC measurement.

Pulse sequences



Extension sequences

decoupling	The default is **TRUE**.
dante_presat	The default is **FALSE**.
tri_mode	Select **Off**, **Presaturation**, or **Homo Decouple**. The default is **Off**.

Parameters

x_domain	Observation nucleus of the f_2 axis. The default is **Proton**.
x_sweep	Observation range of the f_2 axis. The default is **15 ppm**.
x_offset	Observation center of the f_2 axis. The default is **5 ppm**.
x_points	Number of points to sample along the t_2 axis. The default is **1024**.
y_domain	Observation nucleus of the f_1 axis. The default is **Carbon13**.
y_sweep	Observation range of the f_1 axis. The default is **170 ppm**.
y_offset	Observation center of the f_1 axis. The default is **85 ppm**.
y_points	Number of points to sample along the t_1 axis. The defaulit is **256**.

C I

scans	Number of scans to accumulate. The default is **2** scans.
x_prescans	Number of dummy scans. The default is four scans.
x_pulse	90° pulse width of the observation channel (^{1}H). The default is **x90** set in the probe file.
x_atn	Attenuator value **xatn** set in the probe file. Every time 6 dB is added, the pulse width is halved.
y_pulse	90° pulse width of the irradiation channel (^{13}C) of the f_1 axis. The default is **y90_hi** set in the probe file.
y_atn	Attenuator value **yatn** set in the probe file.
j_constant	Value of $^{1}J_{CH}$.. The default is **140 Hz**.
purge	Pulse width of the spin lock purge pulse. The default is **1 ms**.
relaxation_delay	Waiting time between repeated pulses. The default is **1.5 s**.
grad_1_amp	Pulse output of the first FG pulse (PFG1). The default is **35%**.
grad_2_amp	Pulse output of the second FG pulse (PFG2). The default is **10%**.
y_p1_correction	Value to be **e**ntered in the first-order term (P1) of the phase correction of the t_1 axis.

Data processing

The standard process list is **2d_ inverse_ phase_autophase.list**.

How to interpret the spectrum

The f_2 axis represents the ^{1}H chemical shift and the f_1 axis the ^{13}C chemical shift. The correlation signals appear at the points where the perpendicular lines drawn at the peak positions on the f_2 axis and the f_1 axis cross. The correlation signals indicate that corresponding ^{1}H and ^{13}C are directly coupled. All correlation peaks appear in the same phase.

Supplementary note

- In principle, this measurement method makes the peak separation along the f_1 axis and the S/N ratio better than the HMQC measurement. However, the pulse sequences are so complicated that the S/N ratio decreases compared with that of HMQC. In many cases, HMQC is advantageous. Therefore, use this method only when better peak separation along the f_1 axis is required. To utilize the advantage of the HSQC method, you must improve the digital resolution along the f_1 axis a great deal using a large value of **y_points**.
- It is recommended that you stop spinning the sample tube during measurement.

C I

4.3.8 hsqc_tocsy_dec_phase_pfgzz.ex2

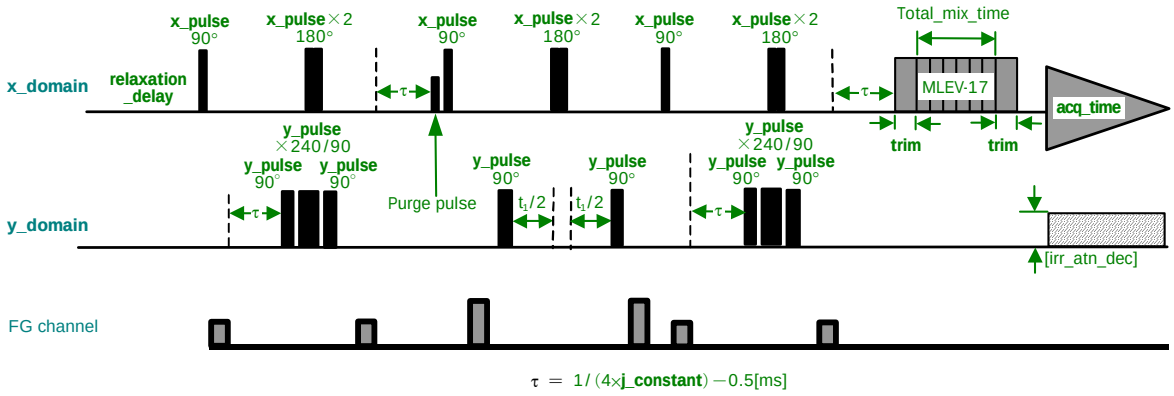
Phase-sensitive PFG HSQC-TOCSY measurement
Directory: /usr/delta/global/experiments/hsqc_tocsy

HSQC is the abbreviation of Heteronuclear Single Quantum Coherence.
TOCSY is the abbreviation of TOtal Correlation SpectroscopY.

Purpose

To observe correlation signals between not only directly coupled ^{1}H and ^{13}C nuclei but also ^{1}H nuclei which belong to the spin network containing that ^{1}H. By observing the ^{1}H nucleus, the S/N ratio is enhanced compared with that achieved using the ^{13}C observation heteronuclear TOCSY method.

Pulse sequences



Extension sequences

decoupling	The default is **TRUE**.
dante_presat	The default is **FALSE**.
tri_mode	Select **Off**, **Presaturation**, or **Homo Decouple**. The default is **Off**.

Parameters

x_domain	Observation nucleus of the f_2 axis. The default is **Proton**.
x_offset	Observation center of the f_2 axis. The default is **5 ppm**.
x_sweep	Observation range of the f_2 axis. The default is **15 ppm**.
x_points	Number of points to sample along the t_2 axis. The default is **1024**.
y_domain	Observation nucleus of the f_1 axis. The default is **Carbon13**.
y_sweep	Observation range of the f_1 axis. The default is **170 ppm**.
y_offset	Observation center of the f_1 axis. The default is **85 ppm**.
y_points	Number of points to sample along the t_1 axis. The default is **256**.
scans	Number of scans to accumulate. The default is **16** scans.
x_prescans	Number of dummy scans. The default is four scans.

C I

x_pulse	90° pulse width of the observation channel (^{1}H). The default is **x90** set in the probe file.
x_atn	Attenuator value **xatn** set in the probe file. Every time 6 dB is added, the pulse width is halved.
y_pulse	90° pulse width of the irradiation channel (^{13}C) of the f_1 axis. The default is **y90_hi** set in the probe file.
y_atn	Attenuator value **yatn** set in the probe file.
j_constant	Coupling constant. The default is **140Hz**.
purge	Pulse width of the spin lock purge pulse. The default is **1 ms**.
x_spinlock_pulse	90° pulse width of the MLEV-17 sequences (spin lock). The default is **x90_spin** set in the probe file.
x_spinlock_atn	Determines the power of the observation channel during spin lock. The attenuator value is **xath_spin** set in the probe file.
trim	Pulse width of the trim pulse. The default is **1 ms**.
mix_time	Mixing time. The default is **50 ms**.
relaxation_delay	Waiting time between repeated pulses. Set it to about 1.3 times T_1 of ^{1}H. The default is 1**.5 s**.
grad_1_amp	Pulse output of the first FG pulse (PFG1). The default is **35%**.
grad_2_amp	Pulse output of the second FG pulse (PFG2). The default is 1**0%**.
y_p1_correction	Value to be **e**ntered in the first-order term (P1) of the phase correction of the t_1 axis.

Data processing

The standard process list is **2d_inverse_phase_autophase.list**.

How to interpret the spectrum

The f_2 axis represents the ^{1}H chemical shift and the f_1 axis the ^{13}C chemical shift. The correlation signals appear at the points where the perpendicular lines drawn at the peak positions on the f_2 axis and the f_1 axis cross. The peaks due to $-CH_3$ and – CH< deflect upward, and those due to $-CH_2-$ deflect downward. The correlation signals between ^{13}C nuclei and not only directly coupled ^{1}H but also ^{1}H nuclei connected to it appear. When the mixing time gets longer, the correlation signals with further separated nuclei appear, although the S/N ratio deteriorates.

Supplementary note

- If the spin lock intensity is too weak, signals over a wide range cannot be spin-locked effectively enough. The spin lock intensity is obtained by the equation shown below and there is no problem if its value is twice the measurement range or more.

$$\text{Spin lock intensity}\,(Hz) = \frac{1}{4 \times \textbf{x\_spinlock\_pulse}}$$

- It is recommended that you stop spinning the sample tube during measurement.
- Too long a spin lock time deteriorates the S/N ratio due to the relaxation time.

C I

4.3.9 inadequate_2d_pfg.ex2

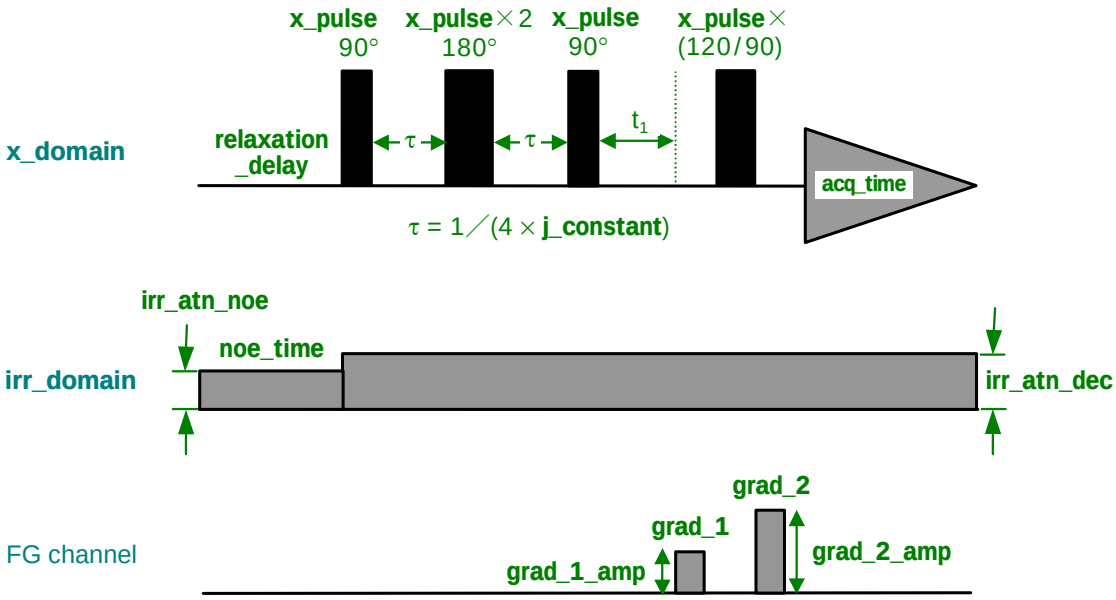
PFG ^{13}C observation two quantum coherence correlation measurement
Directory: **/usr/delta/global/experiments/inadequate**

PFG is the abbreviation of Pulsed Field Gradient.
INADEQUATE is the abbreviation of Incredible Natural Abundance DoublE QUAntum Transfer Experiment.

Purpose of measurement

To observe the connection between ^{13}C and ^{13}C.
Because the sensitivity is very low, it is difficult to measure it. However, if you can acquire data, you can analyze a carbon skeleton directly.

Pulse sequences



Extension sequences

noe	The default is **TRUE**.
decoupling	The default is **TRUE**.

Parameters

x_domain	Observation nucleus. The default is **Carbon13**.
x_offset	Observation center. The default is **100 ppm**.
x_sweep	Observation range of the f_2 axis. The default is **250 ppm**.
x_points	Number of points to sample along the t_2 axis. The default is **2048**.
scans	Number of scans to accumulate (a multiple of 8). The default is **8** scans.
x_prescans	Number of dummy scans. The default is four scans.

C I

y_sweep	Observation range of the f_1 axis. The default is **1.5 × x_sweep**.
y_points	Number of points to sample along the t_1 axis. The default is **64**.
x_pulse	90° pulse width of the observation channel (^{13}C). The default is **x90** in the probe file.
x_atn	Attenuator value **xatn** set in the probe file. Every time 6 dB is added, the pulse width is halved.
j_constant	Value of $^{1}J_{CH}$. The default is **40 Hz**.
relaxation_delay	Waiting time between repeated pulses. The default is **10 s**.
repetition_time	**relaxation_delay+ x_acq_time**.
grad_1	Pulse width of the first FG pulse (PFG1). The default is **1 ms**.
grad_1_amp	Pulse output of the first FG pulse (PFG1). The default is **20%.**
grad_2	Pulse width of the second FG pulse (PFG2). The default is the same as **grad_1.**
grad_2_amp	**P**ulse output of the second FG pulse (PFG2). The default is **grad_1_amp** × **2**.
grad_shape	Waveform of the FG pulse. Select **SQUARE, SINE**, or **GAUSS**. The default is **SINE**.
grad_recover	Recovery time after the FG pulse. The default is **0.1 ms**.

Data processing

The standard process list is **2d_inadequate_abs.list**.

How to interpret the spectrum

The f_2 axis represents the ^{13}C chemical shift. The f_1 axis also represents the ^{13}C chemical shift, but its frequencies double that of the f_2 axis. The symmetrical axis is on the diagonal of the data, but the peaks do not appear on the diagonal. The correlation signals appear between chemically ^{13}C nuclei bonded. Pursuing a pair of the correlation signals reveals the connection of the carbon skeleton.

Supplementary notes

- The intensity of correlation signals depends on the value of **j_constant.**
  It is difficult for a sample having a wide range of J_{cc} values to display all correlation signals using one **j_constant** value. In this case, you need to perform measurement several times with different **j_constant** values.
- It is very effective for a sample having a long relaxation time to add a relaxation reagent, for example, to the sample.

C I

4.3.10 noesy_phase_pfgzz.ex2

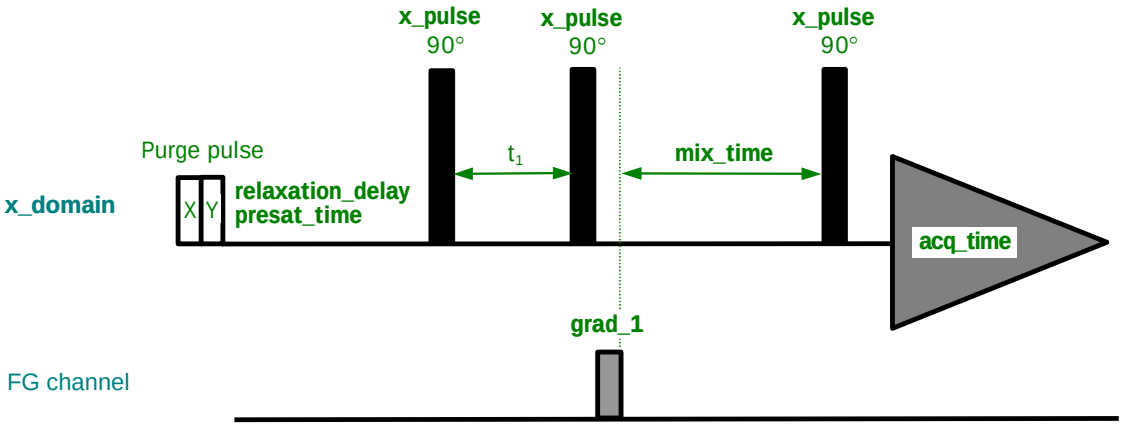
Phase-sensitive detection NOESY measurement
Directory: /usr/delta/global/experiments/noesy

NOESY is the abbreviation of Nuclear Overhauser Effect SpectroscopY.

Purpose of measurement

To observe correlation signals due to NOE and chemical exchange. The spatially nearby nuclei can be identified by observing NOE. This method is useful for three-dimensional structural analysis.

Pulse sequences



Extension sequences

dante_presat	The default is **FALSE**.
irr_mode	Select **Off**, **Presaturation**, or **Homo Decouple**. The default is **Off**.
tri_mode	Select **Off**, **Presaturation**, or **Homo Decouple**. The default is **Off**.

Parameters

x_domain	Observation nucleus. The default is **Proton**.
x_offset	Observation center. The default is **5 ppm**.
x_sweep	Observation range. The default is **15 ppm**.
x_points	Number of points to sample along the t_2 axis. The default is **1024**.
y_points	Number of points to sample along the t_1 axis. The default is **256**.
scans	Number of scans to accumulate (a multiple of 4). The default is **4** scans.
x_prescans	Number of dummy scans. The default is four scans.
x_pulse	90° pulse width of the observation channel (^{1}H). The default is **x90** set in the probe file.

C I

x_atn	Attenuator value **xatn** set in the probe file. Every time 6 dB is added, the pulse width is halved.
mix_time	Mixing time. The default is **500 ms**.
relaxation_delay	Waiting time between repeated pulses. The default is 1.**5 s**.
repetition_time	**relaxation_delay+ x_acq_time**.
grad_1	Pulse width of the PFG1 pulse. The default is 1 **ms**.
grad_1_amp	Pulse output of the PFG1 pulse. The default is **15%**.
y_p1_correction	Value to be **e**ntered in the first-order term (P1) of the phase correction of the t_1 axis.

Data processing

The standard process list is **2d_homo2d_phase_autophase.list**.

How to interpret the spectrum

Both the f_2 axis and the f_1 axis represent ^{1}H chemical shifts. The correlation signals appear at the points where the perpendicular lines drawn at the peak positions on the f_2 axis and the f_1 axis cross. The correlation signals due to the J coupling also appear. To distinguish them, use another method such as the COSY method.

Supplementary note

It may be difficult to observe NOE for samples having medium molecular weights of 1000 to 5000. In this case, use the ROESY method or the phase-sensitive ROESY method.

C I

4.3.11 t_roesy_phase.ex2

Phase-sensitive detection ROESY measurement
Directory: /usr/delta/global/experiments/roesy

T-roesy is the abbreviation of Transverse ROtating frame nuclear Overhauser Effect SpectroscopY.

— CAUTION ———

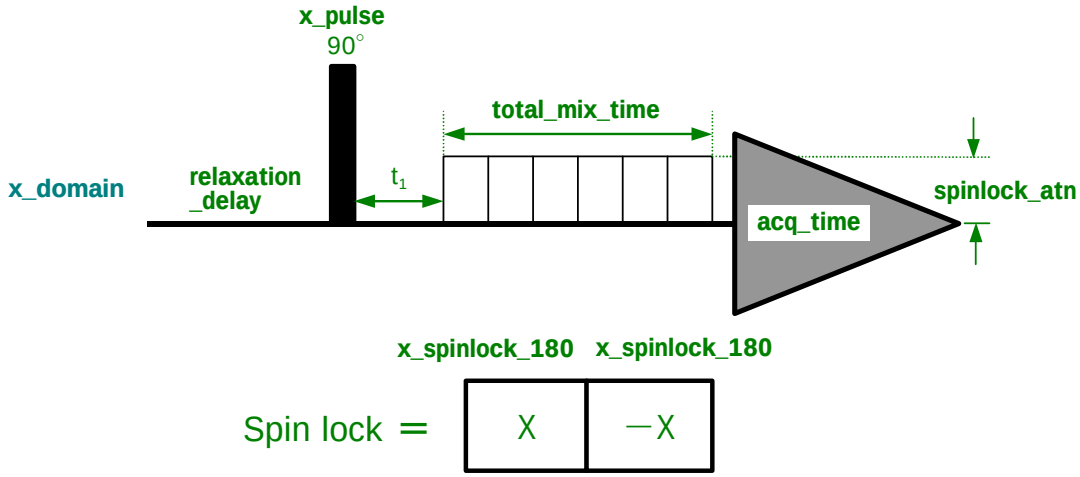
Too large an output (too small a value of attenuator**) can damage the instrument.**

■ Purpose of measurement

To observe correlation signals due to ROE (NOE in a rotating frame).

This method is useful for measuring samples having intermediate molecular weights (1000 to 5000), whose NOE is usually difficult to observe. Nuclei existing spatially close to each other can be determined in the same way as in the NOESY method.

■ Pulse sequences



■ Extension sequences

dante_presat	The default is **FALSE**.
irr_mode	Select **Off**, **Presaturation**, or **Homo Decouple**. The default is **Off**.
tri_mode	Select **Off**, **Presaturation**, or **Homo Decouple**. The default is **Off**.

■ Parameters

x_domain	Observation nucleus. The default is **Proton**.
x_offset	Observation center. The default is **5 ppm**.
x_sweep	Observation range. The default is **15 ppm**.
x_points	Number of points to sample along the t_2 axis. The default is **1024**.

C I

y_points	Number of points to sample along the t_1 axis. The default is **256**.
scans	Number of scans to accumulate (a multiple of 4). The default is **4** scans.
x_prescans	Number of dummy scans. The default is 4 scans.
x_pulse	90° pulse width of the observation channel (^{1}H). The default is **x90** set in the probe file.
x_atn	Attenuator value **xatn** set in the probe file. Every time 6 dB is added, the pulse width is halved.
x_spinlock_mode	Select the mode of the spin lock pulse. The default is **18 dB down**.
x_spinlock_atn	Determines RF output for the spin lock pulse. The default is **x_atn** minus the value selected in **x_spinlock_mode.**
spinlock_strength	Indicates the frequency range to be excited by the spin lock pulse.
mix_time	Mixing time. The default is **250 ms**.
total_mix_time	Mixing time to be actually used.
relaxation_delay	Waiting time between repeated pulses. The default is **1.5 sec**
repetition_time	**relaxation_delay+ x_acq_time**.
y_p1_correction	Value to be **e**ntered in the first-order term (P1) of the phase correction of the t_1 axis.

Data processing

The standard process list is **2d_homo2d_phase_autophase.list**.

How to interpret the spectrum

Both the f_2 axis and the f_1 axis represent ^{1}H chemical shifts. The correlation signals due to ROE appear at the points where the perpendicular lines drawn at the peak positions on the f_2 axis and the f_1 axis cross.

Supplementary note

If the spin lock intensity is too weak, the intensity of signals at the end of the observation range decreases. If it is too strong, not only the correlation signals due to the ROE but also those due to HOHAHA appear.

C I

4.3.12 tocsy_mlev1760_phase.ex2

Phase-sensitive detection TOCSY measurement using the MLEV17 sequence.
Directory: /usr/delta/global/experiments/tocsy

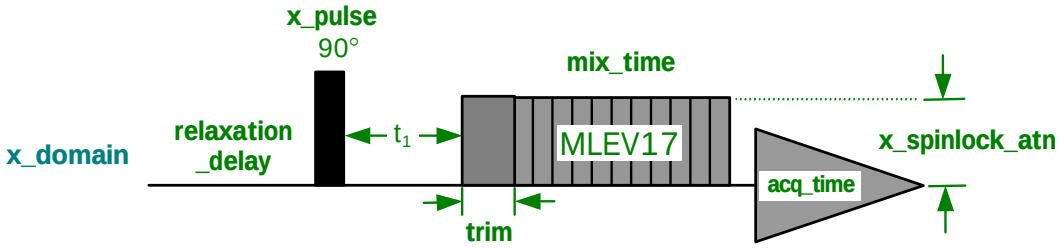
TOCSY is the abbreviation of TOtal Correlation SpectroscopY.
TOCSY is another name for HOHAHA.
HOHAHA is the abbreviation of HOmonuclear HArtmann-HAhn spectroscopy.

Purpose of measurement

To extract a group of peaks (a spin network) connected with each other via J-couplings.

Unlike in the relayed shift correlation method, correlation signals appear non-selectively. The phase-sensitive detection enhances the separation and the S/N ratio of signals.

Pulse sequence



Extension sequences

dante_presat	The default is **FALSE**.
irr_mode	Select **Off**, **Presaturation**, or **Homo Decouple**. The default is **Off**.
tri_mode	Select **Off**, **Presaturation**, or **Homo Decouple**. The default is **Off**.

Parameters

x_domain	Observation nucleus. The default is **Proton**.
x_offset	Observation center. The default is **5 ppm**.
x_sweep	Observation range. The default is **15 ppm**.
x_points	Number of points to sample. The default is **1024**.
scans	Number of scans to accumulate (a multiple of 4). The default is **4** scans.
x_prescans	Number of dummy scans.
y_points	Number of points to sample along the t_1 axis. The default is **256**.
x_pulse	90° pulse width of the observation channel (^{1}H). The default is **x90** set in the probe file.
x_atn	Attenuator value **xatn** set in the probe file. Every time 6 dB is added, the pulse width is halved.

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x_spinlock_pulse	90° pulse width of the spin lock pulse. The value of **x90_spin** in the probe file is set.
x_spinlock_atn	Determines the RF output of the spin lock pulse. The attenuator value is **xatn_spin** set in the probe file.
trim	Pulse width of the trim pulse. The default is **1 ms**.
mix_time	Mixing time. The default is **50 ms**.
relaxation_delay	Waiting time between repeated pulses. The default is **1.5 s**
repetition_time	**relaxation_delay+ x_acq_time**.
mix_time_loop	Number of times to irradiate of the spin lock pulse.
total_mix_time	Mixing time to be actually used.
y_p1_correction	Value to be **e**ntered in the first-order term (P1) of the phase correction of the t_1 axis.

Data processing

The standard process list is **2d_homo2d_phase_autophase.list**.

How to interpret the spectrum

Both the f_2 axis and the f_1 axis represent ^{1}H chemical shifts. The correlation signals appear at the points where the perpendicular lines drawn at the peak positions on the f_2 axis and the f_1 axis cross. When the mixing time gets longer, the correlation signals with further separated nuclei appear, although the S/N ratio deteriorates.

5

MULTINUCLEAR NMR MEASUREMENT

This chapter presents how to observe NMR signals of nuclei other than the ^{1}H and ^{13}C nuclei. Such nuclear NMR is called multinuclear NMR.
Additional functions of the spectrometer and probe are required for multinuclear NMR observation, and preparatory knowledge is necessary. Please read this chapter before you attempt multinuclear NMR measurement for the first time.

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5.1 OUTLINE OF MULTINUCLEAR NMR MEASUREMENT

This section outlines the basics of multinuclear NMR measurement. It includes the definition and features of multinuclear NMR, a discussion of sensitivity on the basis of the ^{13}C nucleus, and a brief description of the hardware composition of the multinuclear NMR observation instrument.

5.1.1 About Multinuclear NMR

The definition and features of multinuclear NMR are explained below.

■ Definition of multinuclear NMR

Multinuclear NMR is defined as all nuclear NMR, except that for the ^{1}H and ^{13}C nuclei, where NMR signals can theoretically be observed.

■ Features of multinuclear NMR

Multinuclear NMR has the following features:

- NMR signals of many nuclei can be easily detected and measured in a shorter time than that for the ^{13}C nucleus, as commonly used in organic chemistry.
- The range of chemical shifts is wide, as the specific nucleus possesses a large mass number, and p electrons and d electrons are present around the atomic nucleus. The sample can be measured even if it is not in solution.
- There are many nuclei with I>1/2 when the nuclear spin I exceeds 1/2.
- The nuclei with I>1/2 possess a quadrupole moment, resulting in short relaxation that gives rise to a wide signal line.
- A fast repetition pulse rate can be used for measurements of nuclei with short relaxation times to shorten the measurement time.

To observe multinuclear NMR, it is necessary to use experimental conditions different from those for ^{1}H and ^{13}C NMR and to have knowledge about the different measurement conditions and ranges of chemical shifts. The various issues you may encounter when measuring multinuclear NMR are explained below.

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5.1.2 Relative Sensitivity of Multinuclear NMR

This section explains multinuclear NMR sensitivity.

■ Detection sensitivity of multinuclear NMR

The detection sensitivity of NMR signals depends on the nuclear magnetic moment, nuclear spin and nuclear spin concentration of the sample. The detection sensitivity under a fixed magnetic field is proportional to the following expression:

$$I(I+1)\times\nu_0^{\,3}\times N$$

where I is the nuclear spin, ν_0 is the resonance frequency, and N is the nuclear spin concentration.

Note that the above expression represents the peak area. Therefore, a peak with a wide line width will not be as high as expected from the above expression, making it difficult to detect. Generally, a nucleus with $I>1/2$ gives rise to a wide line width due to the quadrupole moment, resulting in the detection sensitivity (the peak height) being low. The larger the quadrupole moment is, and the lower the symmetry of the electric field around the observation nucleus is, the wider the line width due to the quadrupole moment becomes.

The value of I and ν_0 are intrinsic to the nucleus, and once the measurement nucleus is decided, these are determined. The value of N depends on the sample concentration and natural abundance. Therefore, to enhance detection sensitivity you need to increase the sample concentration or use an enriched sample. The use of a higher magnetic field SCM is especially effective for nuclei of low resonance frequencies.

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Relative sensitivity of multinuclear NMR

When multinuclear NMR is observed, the detection sensitivity depends substantially on the nucleus. The relative sensitivity as compared to the standard ^{13}C nucleus is used to estimate the degree of difficulty and the necessary time for measurement. The following figure shows the relation between the relative sensitivity and the resonance frequency of different nuclei.

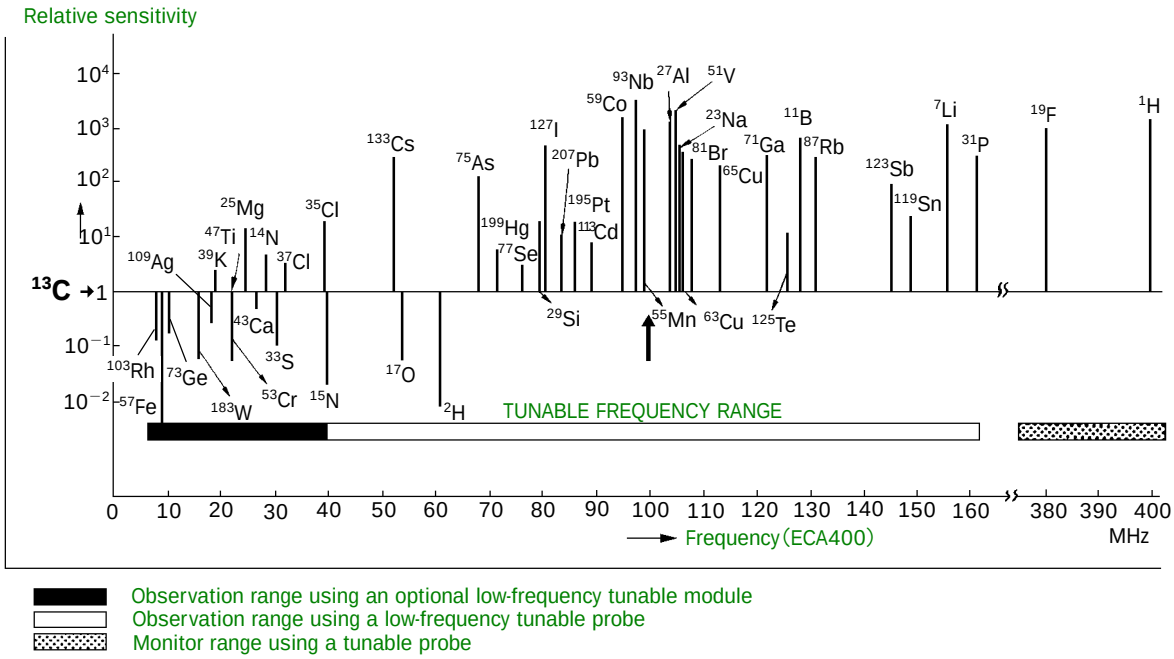

Fig. 5.1 Relative sensitivity of multinuclear observation

Refer to the tables in Section 5.5.1 for information on natural abundance, nuclear spins, and relative sensitivities of nuclei.

C I

5.1.3 Multinuclear NMR Observation Instrument

A block diagram of the basic composition of the multinuclear NMR observation instrument is shown below.

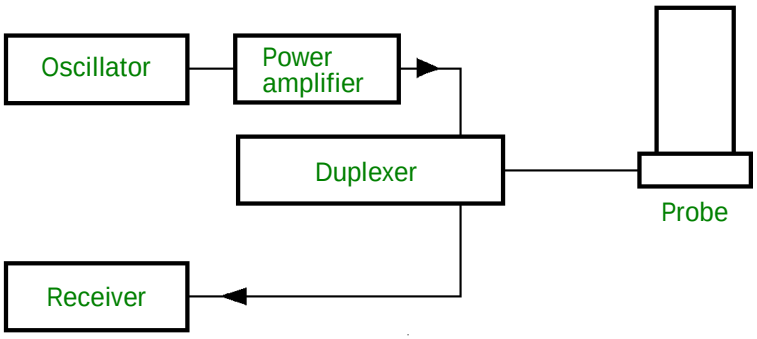

Fig. 5.2 Block diagram of the multinuclear NMR observation instrument

In the multinuclear NMR observation system, the oscillator generates radio waves of specific frequencies and the power amplifier amplifies them. Then, the output power is fed into the probe through the duplexer which allows switching between transmit and receive. The probe is provided with the variable capacitors for tuning and matching to the resonance frequency. Depending on the observation frequency, the small capacitor called the stick may need to be exchanged as one variable condenser can not cover all resonance frequencies.

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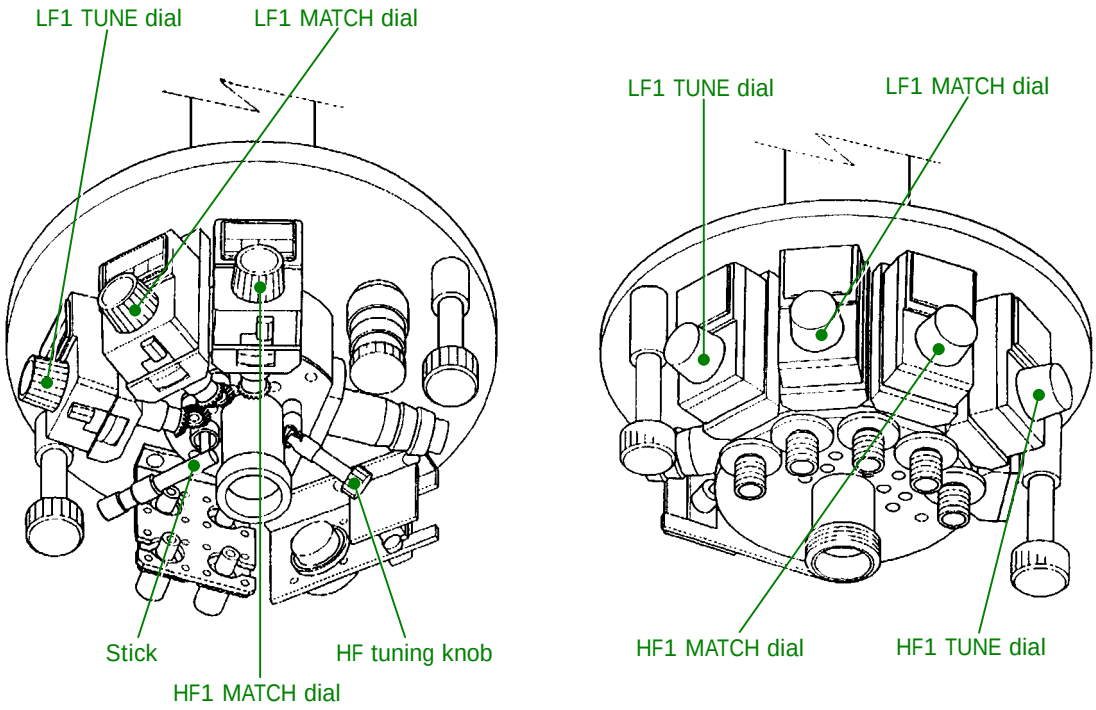
5.2 MULTINUCLEAR NMR MEASUREMENT

This section explains the actual procedures needed to measure multinuclear NMR, and also the ^{2}H nucleus as a special case.

5.2.1 Multinuclear Observation Probes

The probes used for multinuclear NMR measurement are called multinuclear observation probes. The following types of multinuclear probes are available:

- 5 mm TH Tunable Probe (standard)
- 5 mm TH Tunable FG Probe (optional)
- 5 mm TH Auto Tune Probe (optional)
- 5 mm TH Auto Tune FG Probe (optional)
- 10 mm TH Tunable Probe (optional)
- 10 mm TH Auto Tune Probe (optional)
- Low Frequency Tunable Probe (optional)



5 mm TH Tunable Probe

5 mm TH Auto Tune Probe

Fig. 5.3 External appearances of major multinuclear probes

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5.2.2 Operational Procedure for Multinuclear Measurement

1. Load the standard sample into the probe.

Choose a proper standard sample for each nucleus. It is recommended that you use the reference substances as explained in the next section, 5.2.3.

2. Change the observation nucleus.

Set **x domain** in **Acquisition** in the ***Experiment*** window to the observation nucleus.

3. Change to a suitable stick.

Insert a suitable stick referring the table attached the probe. Since the sign of the alphabet of 1 character (A, B, C…) is indicated to a stick, select a stick for the observation nucleus.

☞ Refer to the separate manual, “HANDLING OF HARDWARE”.

4. Set the LF1 MATCH and LF1 TUNE dials to suitable values.

Set MATCH dial to a suitable value which is searched from the graph attached to the probe.

For typical nuclei such as ^{31}P, ^{13}C, ^{29}Si, ^{2}H, ^{17}O and ^{15}N, adjust the TUNE dial value to that shown in the tuning dial table supplied with the probe. For nuclei other than the above, set the value of a nucleus whose dial value is known and whose resonant frequency is close.

5. Measure the pulse width.

Measure the pulse width using the standard sample.

Be sure first to set the peak of the standard sample to the center of the observation frequency and then measure the pulse width (☞Chapter 3). Furthermore, be sure the peak is not folded (☞Section 5.3.4).

6. Set the chemical shift reference.

When using the first standard as the standard sample, record the absolute frequency of the resonant position of the sample. The reference value of the chemical shift becomes zero.

7. Measure the desired sample.

☞ See Section 3.3.

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5.2.3 Chemical Shifts and Reference Substances

■ Definition of a chemical shift

The chemical shift,δ, of a multinuclear NMR sample is given in ppm relative to the reference similarly to ^{1}H and ^{13}C NMR.
The chemical shift is defined in the following equation:

$$\text{Chemical shift}\left(\delta_{ppm}\right)=\frac{\delta-\delta_{ref}}{\delta_{ref}}\times 10^{6} \qquad (3.1)$$

σ: Resonance frequency of sample
σ_{ref}: Resonance frequency of reference

It is noted from this equation that the chemical shift of a peak which appears at a lower frequency (a higher magnetic field) than the reference is given as a negative value ofδ and that which appears at a higher frequency is given as a positive value ofδ.

■ The first reference and second reference

The standard substance used in the above equation is called the first reference substance. Tetramethylsilane (TMS) and other compounds which are widely quoted in the literature are utilized as first reference substances.

Sometimes a solvent signal or the signal from a substance which is easily obtained is used as the chemical shift standard. Such substances are called second reference substances. When you use a second reference substance, you should measure the chemical shift in advance using the first reference substance. If this chemical shift is δ_2, the resonance frequency of the first reference substance is given by the following equation. Then, the chemical shift is given by equation (3.1).

$$\text{Resonance frequency of the first reference} = \frac{\text{resonance frequency of the second reference}}{1+\delta_2\times 10^{-6}} \qquad (3.2)$$

When the chemical shift reference is set to a value other than zero in the data processing program, the above calculation is performed.

■ External reference and internal reference

If the standard peak of the chemical shift is in the spectrum under investigation, the peak is called an internal reference. The peak of a solvent or the peak of a reference substance which is dissolved in the sample is used as the internal reference.

However, in the multinuclear NMR, the range of the chemical shifts may be too wide to measure the peaks of the sample and reference substance simultaneously. Also, the peaks of the sample and reference substance may overlap due to a wide line width. In this case, the absolute frequency of the reference substance peak has been measured in advance and the chemical shift scales can be calibrated with reference to this position. This reference substance peak for the chemical shift is called an external reference.

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Reference substances

There is general agreement that for ^{1}H and ^{13}C NMR, chemical shifts should be given with respect to the tetramethylsilane (TMS) reference.
However, for multinuclear NMR there is at present no definite agreement for most nuclei. It is recommended that you select a reference compound considering the following conditions:

- It is readily available.
- It is commonly used in the literature.
- It is a stable compound like TMS.
- The signal is a readily detectable single line.
- The resonance frequency is independent of pH, temperature and concentration, as much as possible.

In the case of I > 1/2, a compound which is ionized in aqueous solution and gives a narrow line is considered as the most suitable reference substance.
For commonly used reference compounds, refer to the table in Section 5.5.1.

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5.2.4 Observation of Nuclei Having a Resonance Frequency Close to that of the ^{2}H Nucleus

The measurement techniques explained below apply to the following nuclei:

^{199}Hg, ^{171}Yb, ^{75}As, ^{209}Bi, ^{2}H, ^{6}Li, ^{139}La, ^{9}Be, ^{17}O, ^{133}Cs, ^{139}Sb, ^{181}Ta and ^{175}Lu.

■ Difficulties with these measurements

When you observe the ^{2}H nucleus or nuclei having a resonance frequency close to that of the ^{2}H nucleus (61 MHz±5 MHz when using the 400 MHz magnet) while operating the deuterium lock circuit, noise increases due to the interaction of the lock system and the observation system. For this reason, it is necessary to stop the operation of the lock circuit. Since the lock signal cannot be used, adjust the resolution using FID.

If a deuterium solvent can be used, adjust the resolution first using this solvent and then stop the lock circuit to measure the sample.

When you measure a peak with a wide line width, like that of the ^{2}H spectrum of a liquid crystal, adjust the resolution once using deuterium solvent and then measure without readjusting the resolution.

■ Stopping the lock circuit

To stop the lock circuit, turn the ^{2}H OSC off according to the following procedure.

1. Select **Tools** – **Params in** the **Spectrometer control** window.
The **Parameter Tool** window opens.

2. Click on **LOCK_OSC_STATE** in **File** to highlight it.

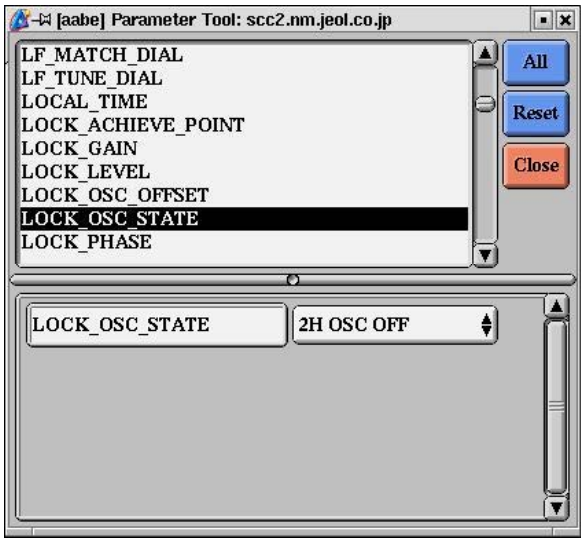

Fig. 5.4 Selecting File in the Parameter Tool window

3. Click on the downward arrow button.
Change display of **2H OSC ON** to **2H OSC OFF**, and turn off ^{2}H LOCK.

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5.2.5 Sensitivity Enhancement by the Pulse Technique

The pulse technique is useful for sensitivity enhancement of nuclei with I = 1/2 that is directly coupled to the proton (^{1}H). Two methods, INEPT (Insensitive Nuclei Enhanced by Polarization Transfer) and DEPT (Distortionless Enhanced by Polarization Transfer), are commonly used. These methods use spin population transfer by applying a combination of pulses to the protons that are directly coupled to the observation nuclei and possess big magnetic moments. The signal enhancement factor (the factor of increase of signal intensity) is much greater than that produced by the nuclear Overhauser effect (NOE), which uses the common proton decoupling method. This is shown in the following table. For example, in the case of the ^{15}N nucleus, the enhancement factor of the signal by NOE is about 4 while it is about 10 when the INEPT or DEPT method is used.

Table 5.1 Signal enhancement factor of observed nuclei resulting from NOE, INEPT, and DEPT

Onserved nucleus	^{11}B	^{13}C	^{15}N	^{29}Si	^{57}Fe	^{103}Rh	^{109}Ag	^{119}Sn	^{183}W
NOE	2.56	2.99	−3.94	−1.52	16.48	−16.89	−9.75	−0.41	13.0.2
INEPT	3.12	3.98	9.87	5.03	30.95	31.77	21.50	2.81	24.04
DEPT									

- The settings of measurement conditions are the same as those for INEPT or DEPT of ^{13}C NMR, but adjust the coupling constant to the ^{1}H nucleus depending on the observation nucleus. For the coupling constants of typical nuclei to ^{1}H, refer to the table shown in Section 5.5.1.
- The measurement mode for INEPT is **hp_inept_dec.ex2**, and that for INEPT is **hp_dept_dec.ex2**.

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5.3 SPECIAL PHENOMENA AND PRECAUTIONS FOR MULTINUCLEAR NMR MEASUREMENT

This section explains various precautions and phenomena to keep in mind when you perform multinuclear NMR measurement.

5.3.1 Precautions for Sample Preparation

■ Selecting a solvent

It is better to use a solvent which does not contain the observed nucleus, if possible. For example, if you measure ^{17}O NMR, use an oxygen-free solvent such as chloroform. If you use a solvent which contains oxygen, such as water (H_2O or D_2O), methanol, acetone or dimethyl sulfoxide, the solvent itself gives rise to a large signal, making signal detection of a low-concentration sample difficult.
You should always keep this type of problem in mind when you perform multinuclear NMR measurement.

■ Using a solid sample

The bigger the sample tube diameter, the more easily powder and pellet samples are filled and measured. Use a sample tube with as big a diameter as possible (usually 10 mm) when performing solid-sample measurement.

■ Using a metallic solid sample

Take the following precautions when performing metal or conductive sample measurement.

An RF pulse applied to a conductive material does not penetrate inside the sample due to the skin effect. Instead, it penetrates only a few microns in from the surface. Therefore, if the sample tube is filled with a normally shaped metal, a spectrum with a good S/N ratio cannot be obtained. To improve the S/N ratio, make a plate sample as thin as possible, a rod sample as slender as possible, or pulverize block samples as finely as possible, so that the surface area of the samples becomes larger.

5.3.2 Selection of Sample Tubes

Common NMR sample tubes are made of glass, which contains compounds of silicon, boron and sodium. Therefore, when ^{29}Si NMR, ^{11}B NMR, and ^{23}Na NMR is performed, the sample tube gives rise to the background signals that are independent of the sample signals under investigation.
Therefore, when it is difficult to distinguish the background signals from the sample signals, a sample tube made of materials which do not contain the nucleus must be prepared. For example, sample tubes made of polymers such as Teflon should be used for ^{29}Si NMR, and sample tubes made of a polymer or quartz should be used for ^{11}B NMR. There is no problem in using a glass sample tube for a ^{23}Na solution, as the line widths of the sample signals are narrow when compared with the background signals from the glass.

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5.3.3 Problems Involved with a Wide Chemical Shift Range

Some signal peaks appear in wide chemical shift ranges in multinuclear NMR, for example, ^{59}Co (15000 ppm) and ^{195}Pt (5000 ppm). The theory behind measurement of such nuclei differs from that of ^{1}H and ^{13}C observations. The problems involved are explained below and in 5.3.4.

■ Chemical shift range

The frequency range where the peaks of the nucleus to be observed appear is called the chemical shift range here. The chemical shift range becomes clear with experience for every nucleus. Generally, the bigger the atomic number and the more d orbital and f orbital electrons the nucleus possesses, the wider the chemical shift range. For the chemical shift ranges of the typical nuclei, refer to Section 5.5.2.

When you measure nuclei that have a wide chemical shift range, you must consider the following three problems:

(a) Signal fold-over
(b) Signal excitation range
(c) Setting of chemical shift reference

Item (a) is explained in Section 5.3.4.
Items (b) and (c) are explained below.

■ Signal excitation range

If the chemical shift range is wide, the 90° pulse sometimes cannot excite all peaks sufficiently and the phase shift cannot be corrected by the first-order equation. As a result, you cannot obtain an in-phase spectrum for all the observation range. In such a case, reduce the flip angle and measure the spectrum. If you reduce the flip angle, shorten **relaxation_delay** to improve the accumulation efficiency.

■ Setting the chemical shift reference

Even if the maximum observation range is set on the instrument, all peaks may not be measured at once. Also, the position of the reference peak for the chemical shift may go out of the observation range. Even in such a case, the chemical shift scale can be set correctly, as the position of the chemical shift reference is recorded as the absolute frequency in the Delta software.

☞ For details, refer to “External reference and internal reference” in Section 5.2.3.

5.3.4 Signal Fold-over

■ Signal fold-over

There are many cases in multinuclear NMR where the chemical shift goes out of the observation range. Also, the peak position may unexpectedly go out of the observation range. In these cases, the peaks which have gone out of the observation range are sometimes observed as fold-over peaks. However, if the signal intensity is strong, the fold-over peaks may not be recognized. When a nucleus or sample is measured for the first time, verify according to the following steps that the peak positions are within the observation range.

1. Maximize the observation range.
2. Change the observation center frequency.
3. Change the value of the electrical filter.

First, maximize the observation range for the measurement. Next, change the observation center frequency.

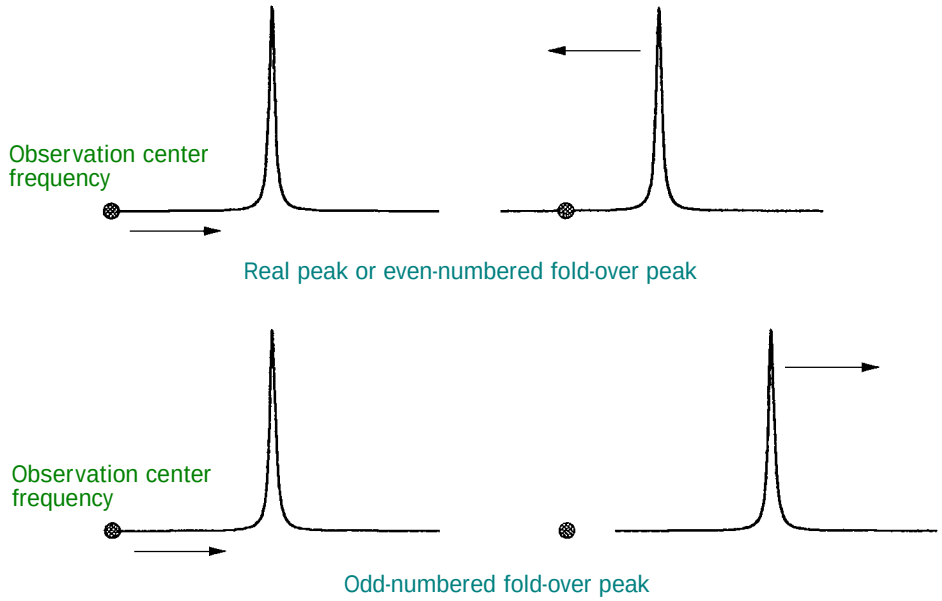

Fig. 5.5 Movement of fold-over peak while the observation center frequency is being changed

Pay attention to the direction of the peak movement. If the peak moves in the same direction as the observation center frequency, it is an odd-numbered fold-over peak. If the peak moves in the opposite direction, it is the real peak or an even numbered fold-over. In this way an odd-numbered fold-over can be recognized.

Next, you need to recognize an even-numbered fold-over. Set the observation center to the peak position. Set the filter value to 1/4 of the observation range and then to the maximum (remove the filter), and compare the peak intensity. If the peak intensity becomes extremely small when the filter value is set to 1/4 of the observation range, it is a fold-over. In this case, move the observation center frequency in the direction that makes the peak intensity stronger, and put the peak in the observation range.

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■ Fold-over of other nuclei

Some nuclei, for example, ^{23}Na and ^{63}Cu, have close resonance frequencies when multinuclear NMR is measured. In this case, a fold-over signal may be mistaken for a real signal, especially if the other nucleus has good sensitivity. Take care when performing measurements of the samples that contain other nuclei with close resonance frequencies.

5.3.5 Problems with Low Frequency Nuclei

When the resonance frequency is low, such as with ^{14}N NMR and ^{73}Ge NMR, the distorted baseline that appears is like a signal with a wide line width. This occurs due to the oscillation of the NMR signal detection coil induced by the observation RF pulse, and is called the acoustic ringing. This false signal should be distinguished from the real one. Distinguish between them using the following two methods.

- Shift the observation center frequency.
  A real peak moves with the observation center frequency while acoustic ringing does not move.
- Put only the solvent into the sample tube and measure it.
  The acoustic ringing appears at almost the same position with the same intensity even when only the solvent without the sample is measured, and thus can be distinguished from the real signal.

It is possible to decrease the acoustic ringing by using the following two methods:

- Make the **delay** time longer.
  Click on the **Expmnt** button in the **Spectrometer Control** window**.**

  The ***Open Experiment*** windowopens. In the **1d/special** directory in this window, the pulse sequences **single_pulse_manual.ex2** and **single_pulse_dec_ manual.ex2** are available for the X nucleus measurement without ^{1}H irradiation and the X nucleus measurement with ^{1}H irradiation, respectively. The acoustic ringing can be decreased by prolonging the time between applying the observation pulse and starting the FID sampling (**dead_time** + **delay**). Usually, fix **dead_time** to 10μs and adjust **delay** to decrease the acoustic ringing. If **delay** is prolonged, the acoustic ringing decreases, but when **delay** approaches T_2 of the peak, the signal intensity decays rapidly. Also, if **delay** is prolonged, the first order phase shift becomes large, causing the baseline waving. This problem can be solved to some extent by phase simulation.

5.3.6 Selecting ^{1}H Decoupling

^{1}H decoupling for nuclei having I > 1/2 is not needed in most cases, as the intrinsic line width is larger than the ^{1}H coupling constant due to the influence of the quadrupole moment. However, ^{1}H decoupling is needed for measurement of the following two nuclei. The ^{14}N nucleus ionized in solution gives a high symmetrical construction and the intrinsic line width becomes so sharp that the ^{1}H coupling constant can be observed. In ^{17}O NMR, directly coupled ^{1}H contributes to the signal line width. Of course, ^{1}H

decoupling is performed for nuclei where I = 1/2 and the sample contains ^{1}H. When ^{1}H decoupling is performed, the following two problems should be considered:

(a) The sample can be heated by the influence of decoupling.
(b) The signal can disappear due to the negative NOE effect.

Problem (a) occurs when a solvent with a high dielectric constant, like an aqueous solution, is used. Problem (b) occurs when a nucleus which possess a negative spin, like ^{15}N or ^{29}Si, is measured. If the above problems occur, use gate decoupling in place of complete decoupling.

5.3.7 Calculating the Pulse Width When There Is No Proper Reference Sample

If you are unable to obtain a reference sample for measuring or to calibrate the pulse width because it is too expensive or for some reason, use the reference sample for a nucleus with a close resonance frequency. The pulse width can be calibrated according to the following equations. From NMR principles, a flip angle, θ, at which the magnetization precesses is given by

$$\theta\,(\text{radian}) = \gamma \times B_1 \times PW$$

where B_1 is the magnetic field produced by an RF pulse, PW is the pulse width, and γ is the nuclear magnetogyric ratio for the observation nucleus. If the sticks are the same (the electric circuits are the same) and the RF power applied to the probes is the same, B_1 is inversely proportional to approximately the 1/2 power of the resonance frequency. Also, γ is proportional to the resonance frequency, therefore the following relation is given.

$$\frac{\theta_A}{\theta_B} = \left(\frac{\nu_A}{\nu_B}\right)^{\frac{1}{2}} \times \frac{PW_A}{PW_B}$$

θ_A, θ_B: Flip angles of nuclei A, B
ν_A, ν_B: Resonance frequencies of nuclei A, B
PW_A, PW_B: Pulse widths of nuclei A, B

If the flip angle is 90° and the corresponding pulse widths are the 90° pulse widths, $PW90_A$ and $PW90_B$,

$$\frac{PW90_B}{PW90_A} = \left(\frac{\nu_A}{\nu_B}\right)^{\frac{1}{2}}$$

Thus, the 90° pulse width is inversely proportional to approximately the 1/2 power of the resonance frequency. From this equation, the lower the resonance frequency of a nucleus, the longer the pulse width. By using a reference sample whose resonance frequency is close to that of the sample under investigation, the pulse width can be calibrated through this equation. However, apply this equation only to measurements from a nucleus where the stick is the same and the resonance frequency is as close as possible.

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5.4 RELAXATION TIMES OF MULTINUCLEI

This section explains the tendencies of the multinuclear relaxation time.
Refer to it for setting the optimum measurement conditions.

5.4.1 General Tendencies of Relaxation Times of Multinuclei

The spin-lattice relaxation time (T_1) and spin-spin relaxation time (T_2) for nuclei with a nuclear spin of 1/2, as represented by the ^{13}C nucleus, are several seconds to more than 10 seconds. The half-height width ($\Delta\nu_{1/2}$) of an observed signal is narrow (within several hertz) as it is the reciprocal of the T_2 relaxation time. On the other hand, T_2 for nuclei with a nuclear spin greater than 1/2 (quadrupolar nuclei) is fast (milliseconds to sub milliseconds) due to quadrupole moment effects. The line width of the observed signal is wider than a few hundred hertz. Generally, the width at half-height ($\Delta\nu_{1/2}$) of the peak of a quadrupolar nuclei in solution is given by the following equation under the condition $\omega_0\tau_C << 1$, where the molecular motion is sufficiently fast.

$$\pi\Delta\nu_{1/2} = \frac{1}{T_1} = \frac{1}{T_2} = \frac{3\pi^2}{10} \bullet \frac{2I+3}{I^2(2I-1)}\left(1+\frac{\eta^2}{3}\right)\left(\frac{e^2Qq}{h}\right)^2 \tau_c$$

I: Nuclear spin
η: Asymmetry parameter of the electric field gradient around the nucleus under investigation
e^2Qq/h: Quadrupolar coupling constant
ω_0: Observation frequency
τ_C: Auto-correlation time of the molecule (approximately equal to the time required for one rotation of the molecule in solution).

From this equation it is seen that the relaxation time of a quadrupolar nucleus depends on η and e^2Qq/h. Since η reflects the magnitude of the electric field gradient around the nucleus, η is greatly dependent on coordination. For example, Be^{2+} ions have a coordination number of four with H_2O molecules in aqueous solution. Because of this, η becomes very small and T_1 increases to about 2 seconds.
For your reference, values of T_1 of several compounds measured in solution or as crystals are shown below.

Table 5.2 Measured values of T_1

Nucleus	Compounds	T_1 measured
^{9}Be (I=−3/2)	Be $(H_2O)_4^{2+}$	1.9 s (76℃)
^{27}Al (I=5/2)	Al $(SO_4)_3^{3-}$	44 ms
	Al $(D_2O)_3^{3+}$	130 ms
^{63}Cu (I=3/2)	CuCl (Powder)	4.7 ms
	CuBr (Powder)	10 ms
	CuI (Powder)	21 ms

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5.4.2 Reference Data for Relaxation Times and Measurement Conditions of Principal Nuclei

As described above, when nuclei with I > 1/2 are placed in an environment with a large electric-field gradient, the line widths of the signals become wide due to quadrupole moment effects. For such nuclei, T_2 is short and the FID (free induction decay) signals after applying the observation pulse decay rapidly. Therefore, large observation ranges and rapid signal acquisitions are required. Actually, with multinuclear NMR measurement, it is important to know the approximate T_1 values of the nucleus under investigation beforehand, in order to estimate the line width and set the pulse width.

The following table collects reference data for measurement conditions for principal nuclei. Relative sensitivities are based on the standard value of the ^{13}C nucleus. For T_1 and T_2, the longest values are shown in the table. For coupling to ^1H, coupling constants can be observed without decoupling for the nuclei marked ○, and cannot be observed without decoupling for the nuclei marked ×.

Table 5.3 Reference data for relaxation times (T_1, T_2) and measurement conditions of principal nuclei

Nucleus	Nuclear spin	Relative sensitivity	Approx. value of T_1, T_2 (s)	Coupling to ^1H	Chemical shift	Flip angle	Repetition time
^2H	1	0.008	7	○	20 ppm	45°	2 s
^7Li	3/2	1.537	1	×	None	90°	1 s
^{11}B	3/2	754	1	○	200 ppm	90°	1 s
^{13}C	1/2	1.000	10	○	300 ppm	Approx. 45°	2 s
^{14}N	1	5.7	1	○×	600 ppm	90°	1 s
^{15}N	−1/2	0.022	10-100	○	600 ppm	Approx. 45°	4 s
^{17}O	5/2	0.06	1	○×	800 ppm	90°	0.2 s
^{19}F	1/2	4.729	10	○	700 ppm	Approx. 45°	2 s
^{23}Na	3/2	523	1	×	None	90°	1 s
^{27}Al	5/2	1,173	1	×	300 ppm	90°	0.2 s
^{29}Si	−1/2	2.1	20	○	300 ppm	Approx. 45°	2 s
^{31}P	1/2	376	10	○	600 ppm	Approx. 45°	2 s
^{35}Cl	3/2	20.4	1	×	None	90°	1 s
^{39}K	3/2	2.68	1	×	None	90°	1 s
^{59}Co	7/2	1,570	1	×	15,000 ppm	90°	0.2 s
^{109}Ag	−1/2	0.28	100	×	600 ppm	Approx. 45°	4 s
^{113}Cd	−1/2	7.5	20	○	1,000 ppm	Approx. 45°	2 s
^{119}Sn	−1/2	25.6	10	○	600 ppm	Approx. 45°	2 s
^{195}Pt	1/2	18.9	1	○	6,000 ppm	Approx. 45°	1 s
^{199}Hg	1/2	5.5	10	○	4,000 ppm	Approx. 45°	2 s

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Repetition time = FID acquisition time (x_acq_time) + Repetition pulse waiting time (relaxation_delay)

Observation range (FR) = Chemical shift range × Resonance frequency

Example: ^{113}Cd NMR (^{1}H resonance frequency of 400 MHz)

FR = 1,000 ppm × 88.676 MHz = 88.7 kHz

5.5 CHARTS AND MEASUREMENT MODES FOR MULTINUCLEAR NMR MEASUREMENTS

This section contains useful data for multinuclear NMR measurements.

5.5.1 Relationships Between Nuclear Species and Sticks

Sticks used with the TH5 probe are indicated in the table.
For sticks used with other probes, refer to the tables supplied with each probe.

- **Stick**

A,B,C,D,X,Y: Insert the specified stick for measurement.
NO: Remove the stick for measurement.
HF: Measure using the irradiation channel, independently of a stick.
LO: An optional low-frequency observation probe is required for observation.

- **Relative sensitivity**

The ^{13}C sensitivity reference is taken as 1.00.

For measurement of ^{19}F, an optional ^{19}F observation system is required.

Table 5.4 Sticks used for observed nuclei

Nucleus	Stick				Natural abundance, percent	Nuclear spin	Relative sensitivity	Reference	Solvent	J_{XH} range
	300	400	500	600						
^{1}H	HF	HF	HF	HF	99.985	1/2	5.7×10^{3}	$(CH_3)_4Si$	$CDCl_3$	—
^{2}H	A	A	A	A	1.5×10^{-2}	1	8.2×10^{-3}	$(CH_3)_4Si$	$CDCl_3$	—
^{3}H	—	—	—	—		1/2	6.9×10^{3}	$(CH_3)_4Si$	$CDCl_3$	—
^{6}Li	A	A	A	A	7.42	1	3.58	LiCl	D_2O	—
^{7}Li	X	X	X	X	92.58	3/2	1.5×10^{3}	LiCl	D_2O	—
^{9}Be	B	A	B	A	100	−3/2	7.9×10^{1}	$Be(NO_3)_2$	D_2O	—
^{10}B	C	B	D	C	19.58	3	2.2×10^{1}	$NaBH_4$	D_2O	—
^{11}B	NO	NO	X	X	80.42	3/2	7.54×10^{2}	$NaBH_4$	D_2O	30～182
^{13}C	NO	NO	NO	NO	1.108	1/2	1.00	$(CH_3)_4Si$	$CDCl_3$	—
^{14}N	LO	LO	LO	LO	99.63	1	5.7	CH_3NO_2	$CDCl_3$	60～140
^{15}N	D	C	D	D	0.37	−1/2	2.2×10^{-2}	CH_3NO_2	$CDCl_3$	60～140
^{17}O	B	A	B	B	3.7×10^{-2}	−5/2	6.1×10^{-2}	D_2O	D_2O	80～85
^{19}F	HF	HF	HF	HF	100	1/2	4.7×10^{3}	CF_3COOH	$CDCl_3$	—
^{23}Na	NO	NO	X	NO	100	3/2	5.25×10^{2}	NaBr	D_2O	—
^{25}Mg	LO	LO	LO	LO	10.13	−5/2	1.5	$MgCl_2$	D_2O	—
^{27}Al	NO	NO	NO	NO	100	5/2	1.7×10^{2}	$Al(NO_3)_3$	D_2O	110～185
^{29}Si	NO	NO	NO	NO	4.70	−1/2	2.1	$(CH_3)_4Si$	$CDCl_3$	150～420

C I

Nucleus	Stick				Natural abundance, percent	Nuclear spin	Relative sensitivity	Reference	Solvent	J_{XH} range
	300	400	500	600						
^{31}P	X	X	X	X	100	1/2	3.77×10^{2}	H_3PO_4	D_2O	40～1100
^{33}S	LO	LO	LO	LO	0.76	3/2	9.7×10^{-2}	$(NH_4)_2SO_4$	D_2O	—
^{35}Cl	D	LO	LO	LO	75.53	3/2	2.2	KCl	D_2O	41 (HCl)
^{37}Cl	LO	LO	LO	LO	24.47	3/2	3.8	KCl	D_2O	41 (HCl)
^{39}K	LO	LO	LO	LO	93.10	3/2	2.7	KBr	D_2O	—
^{41}K	LO	LO	LO	LO	6.86	3/2	3.3×10^{-2}	KBr	D_2O	—
^{43}Ca	LO	LO	LO	LO	0.145	−7/2	5.27×10^{-2}	$CaCl_2$	D_2O	—
^{45}Sc	NO	NO	NO	NO	100	7/2	1.7×10^{3}	$ScCl_3$	D_2O	—
^{47}Ti	LO	LO	LO	LO	7.28	−5/2	0.87	$TiCl_4$	—	—
^{49}Ti	LO	LO	LO	LO	5.51	−7/2	1.18	$TiCl_4$	—	—
^{50}V	D	LO	LO	LO	0.24	6	0.75	$VOCl_3$	C_6D_6	—
^{51}V	NO	NO	X	NO	99.76	7/2	2.15×10^{3}	$VOCl_3$	C_6D_6	—
^{53}Cr	LO	LO	LO	LO	9.55	−3/2	0.49	$CrO_4(NH_4)_2$	D_2O	—
^{55}Mn	NO	NO	NO	NO	100	5/2	9.94×10^{2}	$KMnO_4$	D_2O	—
^{57}Fe	LO	LO	LO	LO	2.19	1/2	4.2×10^{-3}	$Fe(CO)_5$	C_6D_6	—
^{59}Co	NO	NO	NO	NO	100	7/2	1.57×10^{3}	$K_3Co(CN)_6$	D_2O	—
^{61}Ni	LO	LO	LO	LO	1.19	−3/2	0.24	$Ni(CO)_4$	C_6D_6	—
^{63}Cu	NO	NO	X	NO	69.09	3/2	3.65×10^{2}	CuCN	D_2O	—
^{65}Cu	NO	NO	X	Y	30.91	3/2	2.01×10^{2}	CuCN	D_2O	—
^{67}Zn	LO	LO	LO	LO	4.11	5/2	0.665	$Zn(NO_3)_2$	D_2O	—
^{69}Ga	NO	NO	NO	NO	60.4	3/2	2.73×10^{2}	$Ga(NO_3)_3$	D_2O	—
^{71}Ga	NO	NO	X	X	39.6	3/2	3.19×10^{2}	$Ga(NO_3)_3$	D_2O	—
^{73}Ge	LO	LO	LO	LO	7.76	−9/2	0.617	$Ge(CH_3)_4$	C_6D_6	97.6 (GeH_4)
^{75}As	A	NO	A	A	100	3/2	1.43×10^{2}	$NaAsF_6$	—	90～555
^{77}Se	NO	NO	NO	NO	7.58	1/2	3.0	$Se(CH_3)_2$	C_6D_6	40～65
^{79}Br	NO	NO	NO	NO	50.54	3/2	2.26×10^{2}	NaBr	D_2O	62 (Hbr)
^{81}Br	NO	NO	X	Y	49.46	3/2	2.77×10^{2}	NaBr	D_2O	62 (Hbr)
^{85}Rb	D	LO	LO	LO	72.15	5/2	4.3×10^{1}	RbCl	D_2O	—
^{87}Rb	NO	X	X	X	27.85	3/2	2.77×10^{2}	RbCl	D_2O	—
^{87}Sr	LO	LO	LO	LO	7.02	−9/2	1.1	$SrCl_2$	D_2O	—
^{89}Y	LO	LO	LO	LO	100	−1/2	0.668	$Y(NO_3)_3$	D_2O	—
^{91}Zr	LO	LO	LO	LO	11.23	−5/2	6.04	$(C_2H_5)_2ZrCl_2$	—	—
^{93}Nb	NO	NO	NO	NO	100	9/2	2.74×10^{3}	$NbCl_6$	CD_3CN	—
^{95}Mo	LO	LO	LO	LO	15.72	5/2	2.9	Na_2MoO_4	D_2O	—

C I

Nucleus	Stick				Natural abundance, percent	Nuclear spin	Relative sensitivity	Reference	Solvent	J_{XH} range
	300	400	500	600						
^{97}Mo	LO	LO	LO	LO	9.46	−5/2	1.8	Na_2MoO_4	D_2O	—
^{99}Ru	LO	LO	LO	LO	12.72	−3/2	0.83	RuO_4	—	—
^{101}Ru	LO	LO	LO	LO	17.07	−5/2	1.56	RuO_4	—	—
^{103}Rh	LO	LO	LO	LO	100	−1/2	0.18	$RhCl_6^{3-}$	D_2O	15～30
^{105}Pb	LO	LO	LO	LO	22.23	−5/2	1.41	K_2PdCl_6	D_2O	—
^{107}Ag	LO	LO	LO	LO	51.82	−1/2	0.2	$AgNO_3$	D_2O	—
^{109}Ag	LO	LO	LO	LO	48.18	−1/2	0.28	$AgNO_3$	D_2O	—
^{111}Cd	NO	NO	NO	NO	12.75	−1/2	6.9	$Cd(CH_3COO)_2$	D_2O	—
^{113}Cd	NO	NO	NO	NO	12.26	−1/2	7.6	$Cd(CH_3COO)_2$	D_2O	—
^{113}In	NO	NO	NO	NO	4.28	9/2	8.4×10^1	$In(NO_3)_3$	D_2O	—
^{115}In	NO	NO	NO	NO	95.72	9/2	1.9×10^3	$In(NO_3)_3$	D_2O	—
^{117}Sn	NO	X	X	X	7.61	−1/2	2.0×10^1	$(CH_3)_4Sn$	$CDCl_3$	110～2450
^{119}Sn	X	X	X	X	8.58	−1/2	2.5×10^1	$(CH_3)_4Sn$	$CDCl_3$	110～2450
^{121}Sb	NO	NO	NO	NO	57.25	5/2	5.2×10^1	$KSbCl_6$	CD_3CN	—
^{123}Sb	B	A	B	B	42.75	7/2	1.11×10^1	$KSbCl_6$	CD_3CN	—
^{123}Te	NO	NO	X	NO	6.99	−1/2	1.3×10^1	$(CH_3)_2Te$	C_6D_6	—
^{125}Te	NO	NO	X	X	0.87	−1/2	0.89	$(CH_3)_2Te$	C_6D_6	—
^{127}I	NO	NO	NO	NO	100	5/2	5.30×10^2	Kl	D_2O	—
^{129}Xe	NO	NO	X	Y	26.44	1/2	3.2×10^1	Xe(Gas)	—	—
^{133}Cs	B	A	B	B	100	7/2	2.69×10^2	$CsNO_3$	D_2O	—
^{135}Ba	D	LO	LO	LO	6.59	3/2	1.8	$BaCl_2$	D_2O	—
^{137}Ba	C	B	D	C	11.32	3/2	4.4	$BaCl_2$	D_2O	—
^{139}La	B	A	B	A	99.911	7/2	3.4×10^2	$LaCl_3$	D_2O	—
^{141}Pr	NO	NO	X	Y	100	5/2	1.7×10^5	—	—	—
^{143}Nd	LO	LO	LO	LO	12.18	−7/2	2.33×10^2	—	—	—
^{145}Nd	LO	LO	LO	LO	8.30	−7/2	3.7×10^1	—	—	—
^{147}Sm	LO	LO	LO	LO	15.0	−7/2	1.25×10^2	—	—	—
^{149}Sm	LO	LO	LO	LO	13.8	−7/2	5.9×10^1	—	—	—
^{151}Eu	NO	NO	NO	NO	47.8	5/2	4.8×10^4	—	—	—
^{153}Eu	C	B	D	C	52.2	5/2	4.5×10^3	—	—	—
^{155}Gd	LO	LO	LO	LO	14.80	−3/2	2.3×10^1	—	—	—
^{157}Gd	LO	LO	LO	LO	15.65	−3/2	5.2×10^1	—	—	—
^{159}Tb	NO	NO	NO	NO	100	3/2	3.3×10^4	—	—	—
^{161}Dy	LO	LO	LO	LO	18.9	5/2	4.5×10^1	—	—	—

C I

Nucleus	Stick				Natural abundance, percent	Nuclear spin	Relative sensitivity	Reference	Solvent	J_{XH} range
	300	400	500	600						
^{163}Dy	LO	LO	LO	LO	24.9	5/2	1.6×10^{1}	—	—	—
^{165}Ho	NO	NO	NO	NO	100	7/2	1.0×10^{5}	—	—	—
^{167}Er	LO	LO	LO	LO	22.95	−7/2	6.6×10^{1}	—	—	—
^{169}Tm	LO	LO	LO	LO	100	−1/2	3.2	—	—	—
^{171}Yb	A	NO	A	NO	14.31	1/2	5.46×10^{-3}	—	—	—
^{173}Yb	LO	LO	LO	LO	16.13	−5/2	1.33×10^{-3}	—	—	—
^{175}Lu	C	B	C	C	97.41	7/2	3.12×10^{-2}	—	—	—
^{177}Hf	LO	LO	LO	LO	18.5	7/2	6.38×10^{-4}	—	—	—
^{179}Hf	LO	LO	LO	LO	13.75	−9/2	2.16×10^{-4}	—	—	—
^{181}Ta	B	B	C	C	99.988	7/2	2.0×10^{2}	$KTaCl_6$	—	—
^{183}W	LO	LO	LO	LO	14.40	1/2	6×10^{-2}	Na_2WO_4	D_2O	30～80
^{185}Re	NO	NO	NO	NO	37.07	5/2	2.8×10^{2}	$KReO_4$	D_2O	—
^{187}Re	NO	NO	NO	NO	62.93	5/2	4.9×10^{2}	$KReO_4$	D_2O	—
^{187}Os	LO	LO	LO	LO	1.64	1/2	1.1×10^{-3}	OsO_4	—	—
^{189}Os	LO	LO	LO	LO	16.1	3/2	2.1	OsO_4	—	—
^{191}Ir	LO	LO	LO	LO	37.3	3/2	2.0×10^{-2}	—	—	—
^{193}Ir	LO	LO	LO	LO	62.7	3/2	5×10^{-2}	—	—	—
^{195}Pt	NO	NO	NO	NO	33.8	1/2	1.9×10^{1}	Na_2PtCl_4	D_2O	700～1300
^{197}Au	LO	LO	LO	LO	100	3/2	6×10^{-2}	—	—	—
^{199}Hg	A	NO	A	NO	16.84	1/2	5.4	$(CH_3)_2Hg$	C_6D_6	—
^{201}Hg	LO	LO	LO	LO	13.22	−3/2	1.1	$(CH_3)_2Hg$	C_6D_6	—
^{203}Tl	—	—	—	—	29.50	1/2	2.89×10^{2}	$Tl(NO_3)_3$	D_2O	—
^{207}Pb	NO	NO	NO	NO	22.6	1/2	1.18×10^{1}	$Pb(NO_3)_2$	D_2O	—
^{209}Bi	A	A	A	A	100	9/2	7.77×10^{2}	$Bi(NO_3)_3$	—	—

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5.5.2 Multinuclear NMR Chemical Shifts

The main reason to perform multinuclear NMR is to determine chemical shift values. Unfortunately, it may take a considerable amount of time to find a signal of a new nucleus or an unknown sample due to the wide chemical shift ranges in multinuclear NMR. This is especially true when measuring a new nucleus or an unknown sample. However, if the chemical shift range for the nucleus or sample under study can be estimated, or if the chemical shift value of a similar compound is known, the time required to find the signal can be substantially reduced.

To assist in this estimation, reported experimental data for chemical shift ranges of the following nuclei are shown below: ^{11}B, ^{13}C, ^{14}N/^{15}N, ^{17}O, ^{19}F, ^{27}Al, ^{29}Si, ^{31}P, ^{33}S, ^{59}Co, ^{67}Zn, ^{75}As, ^{77}Se, ^{103}Rh, ^{109}Ag, ^{113}Cd, ^{119}Sn, ^{195}Pt, ^{199}Hg, ^{207}Pb. The vertical lines in the figure show the positions of the signals. If the signal has two or more lines, these are also indicated.
When you measure a new nucleus or an unknown sample, it is recommended that you use these chemical shift figures.

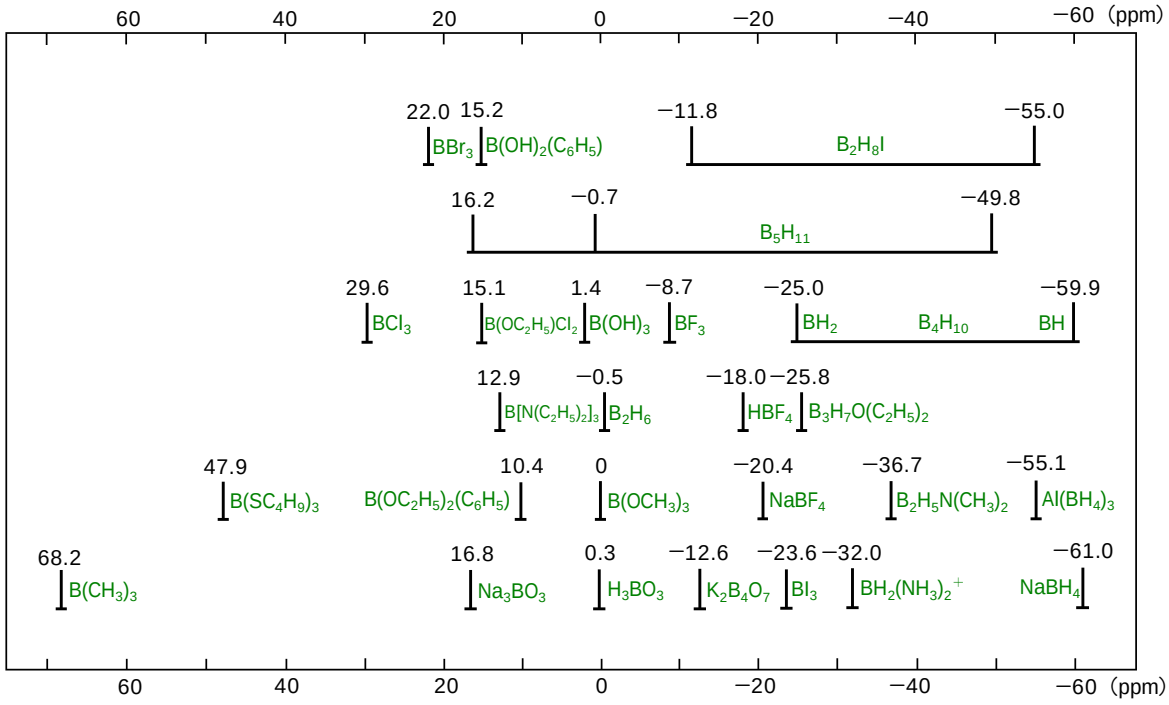

Fig. 5.6 ^{11}B chemical shifts

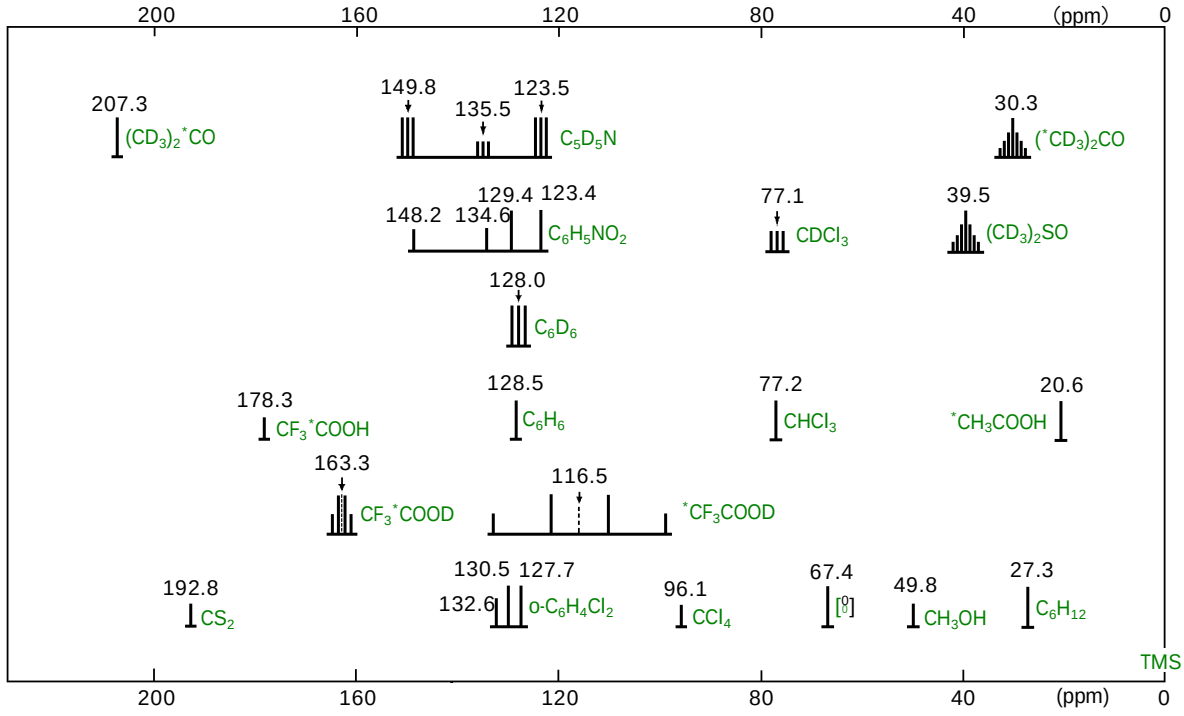

Fig. 5.7 ^{13}C chemical shifts

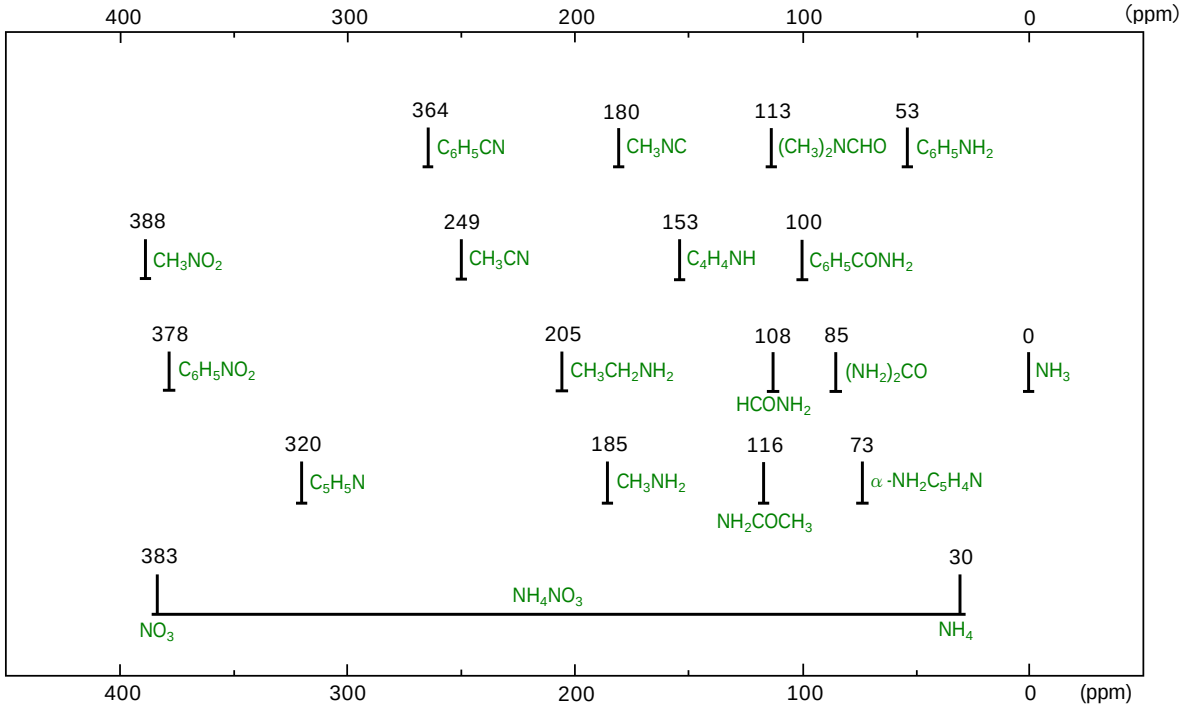

Fig. 5.8 ^{14}N/^{15}N chemical shifts

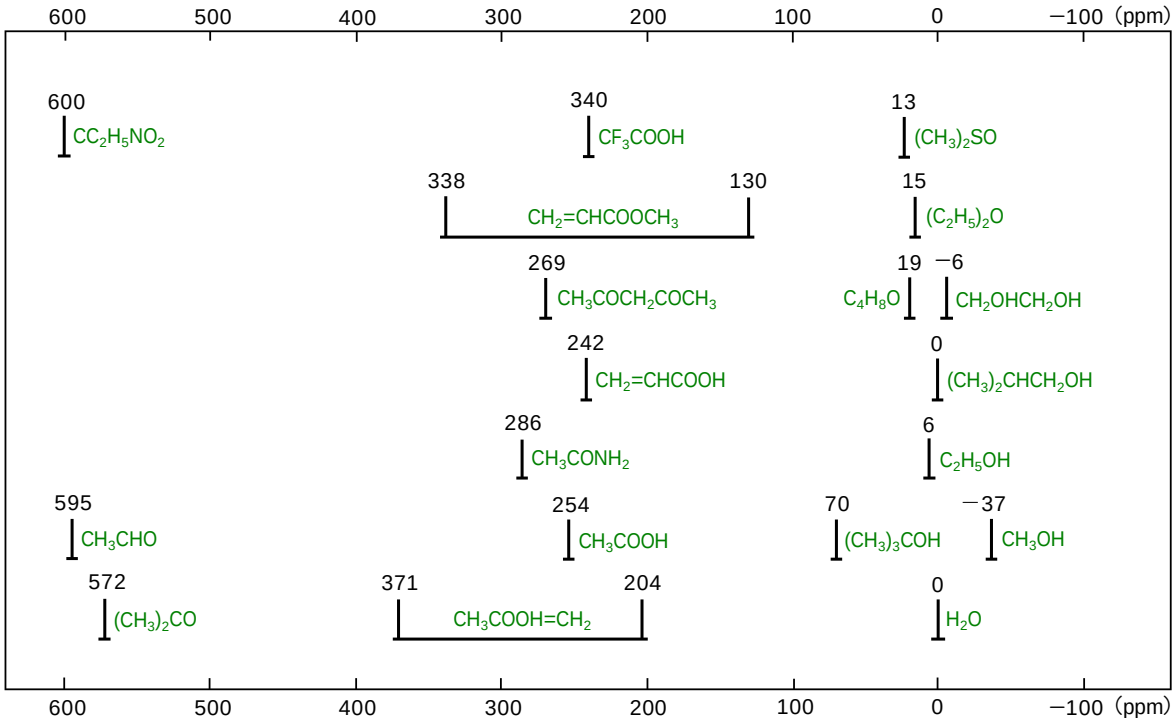

Fig. 5.9 ^{17}O chemical shifts

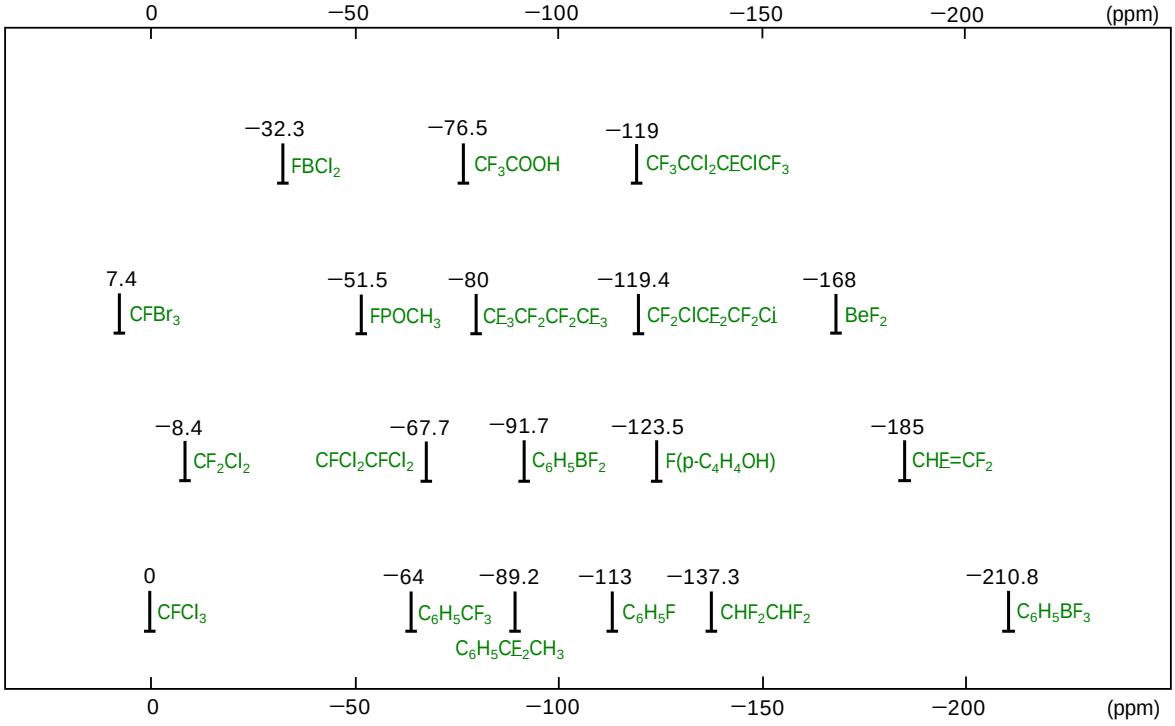

Fig. 5.10 ^{19}F chemical shifts

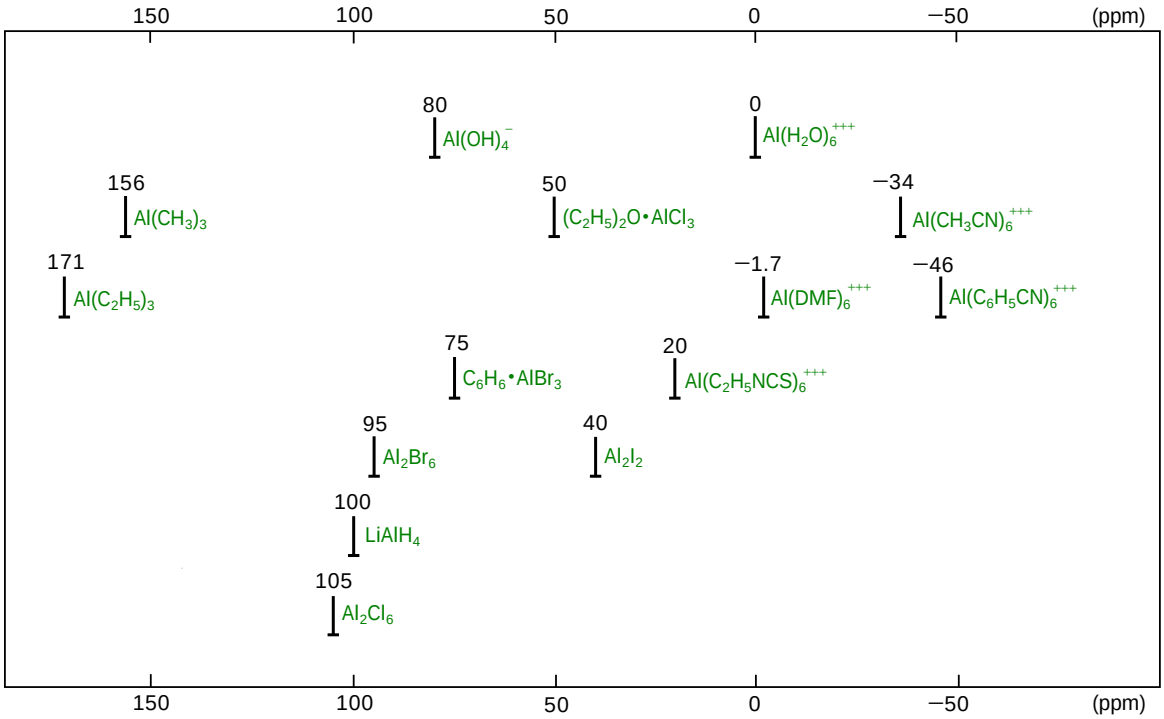

Fig. 5.11 ^{27}Al chemical shifts

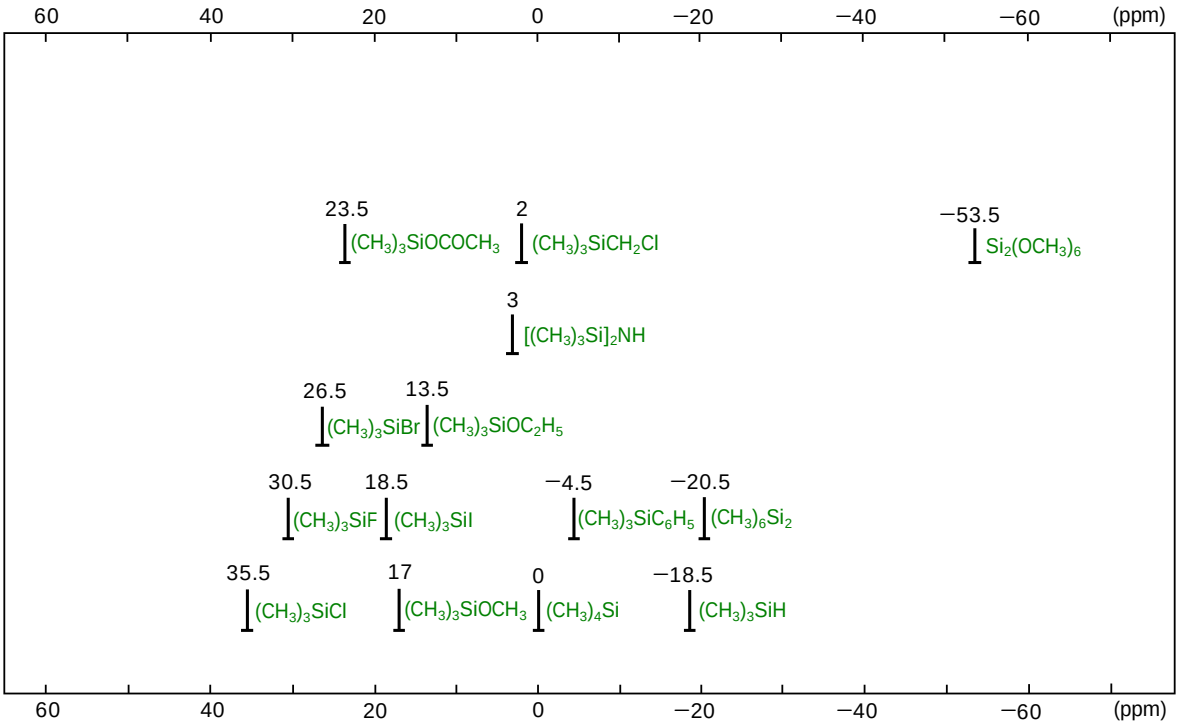

Fig. 5.12 ^{29}Si chemical shifts

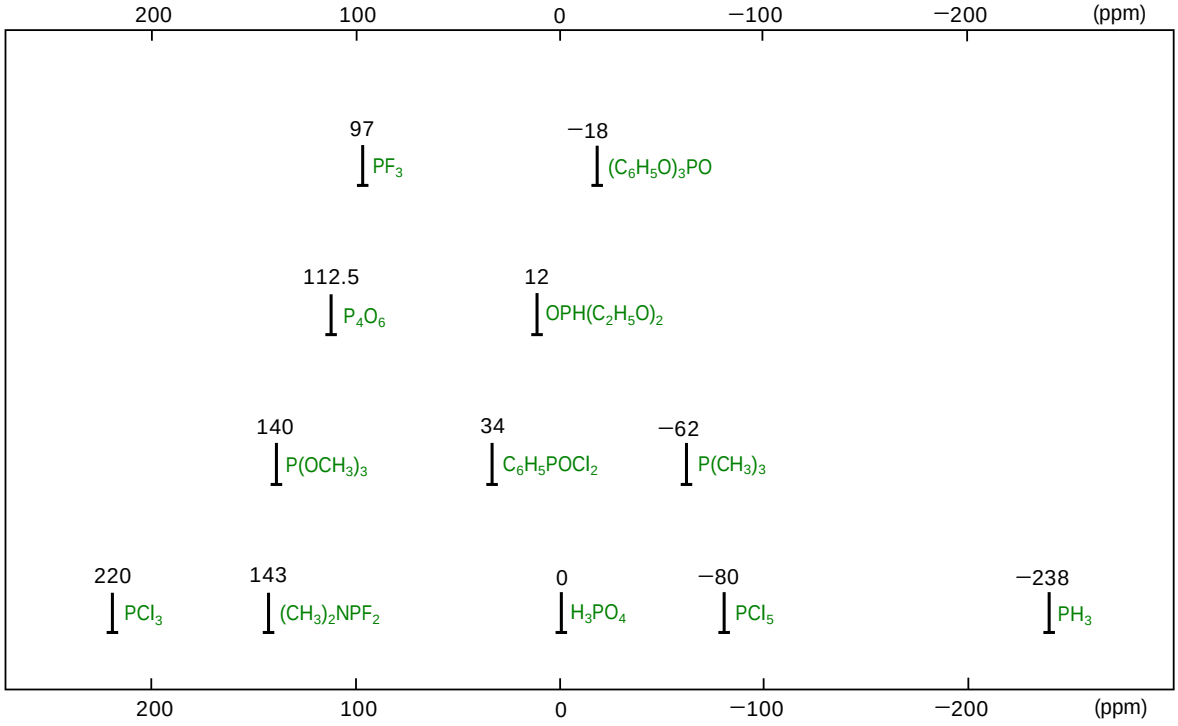

Fig. 5.13 ^{31}P chemical shifts

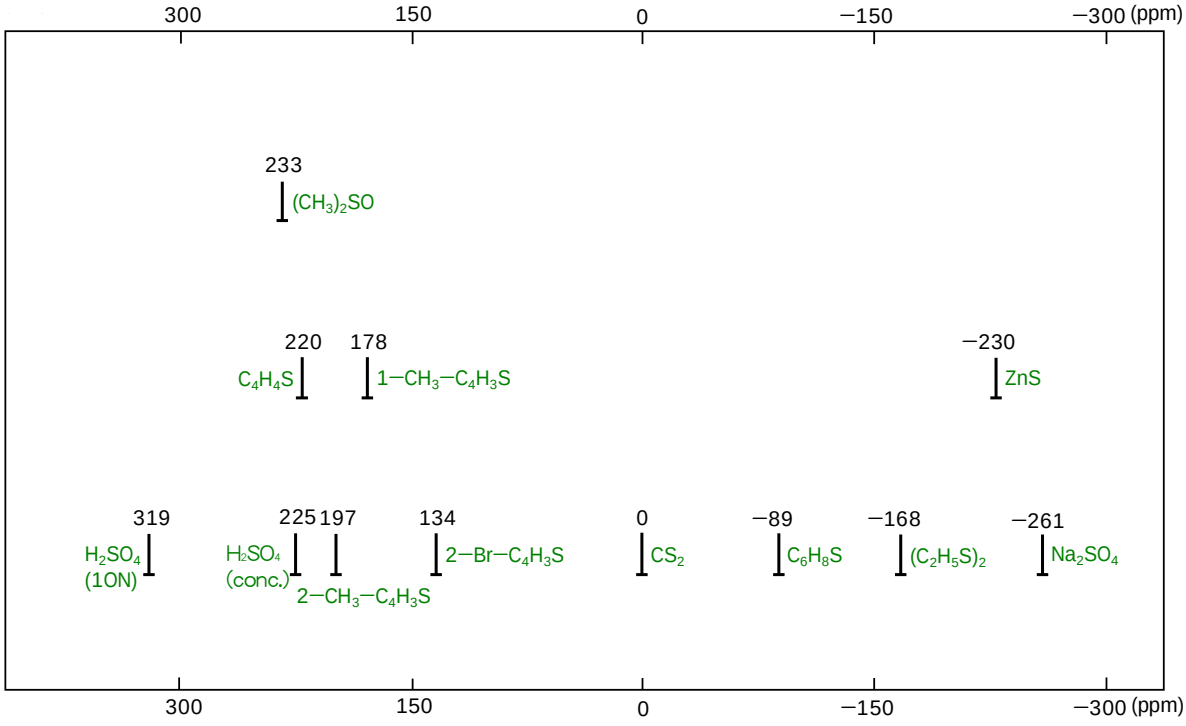

Fig. 5.14 ^{33}S chemical shifts

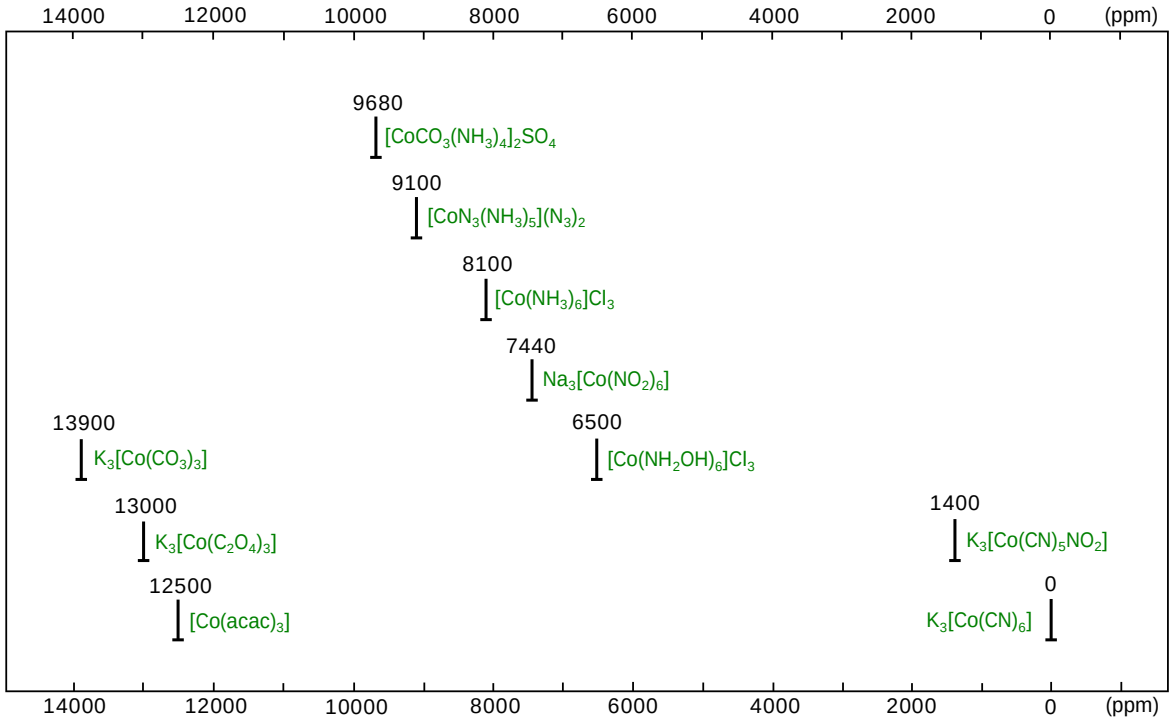

Fig. 5.15 ^{59}Co chemical shifts

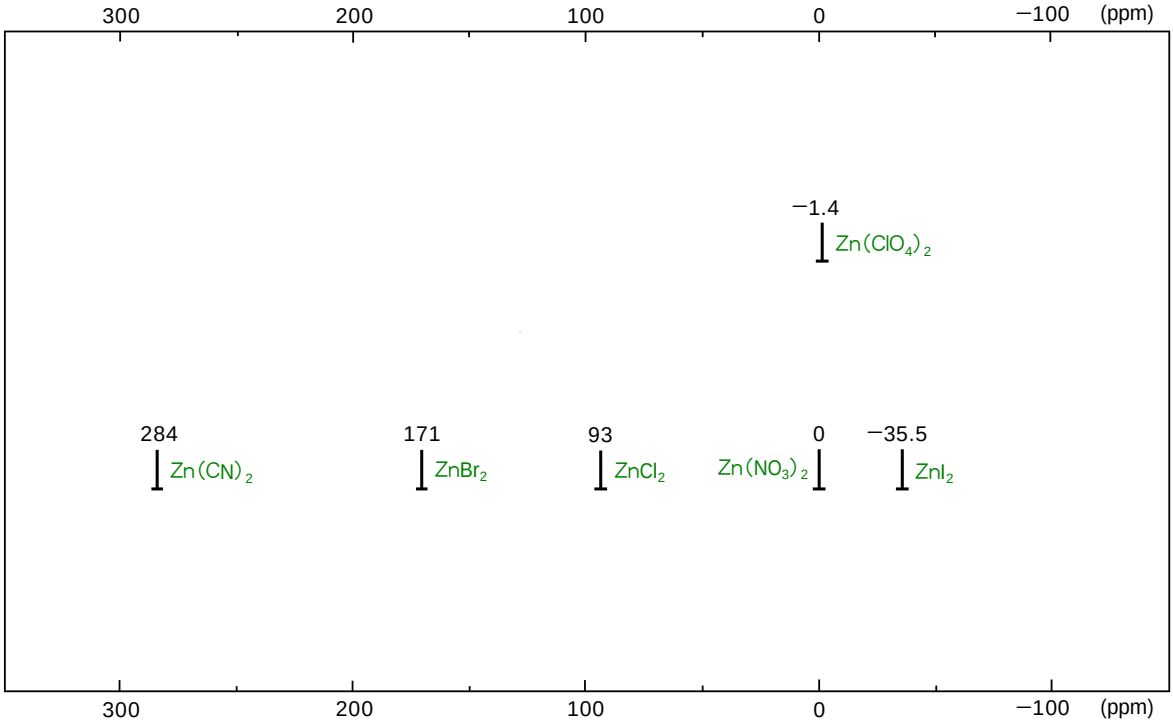

Fig. 5.16 ^{67}Zn chemical shifts

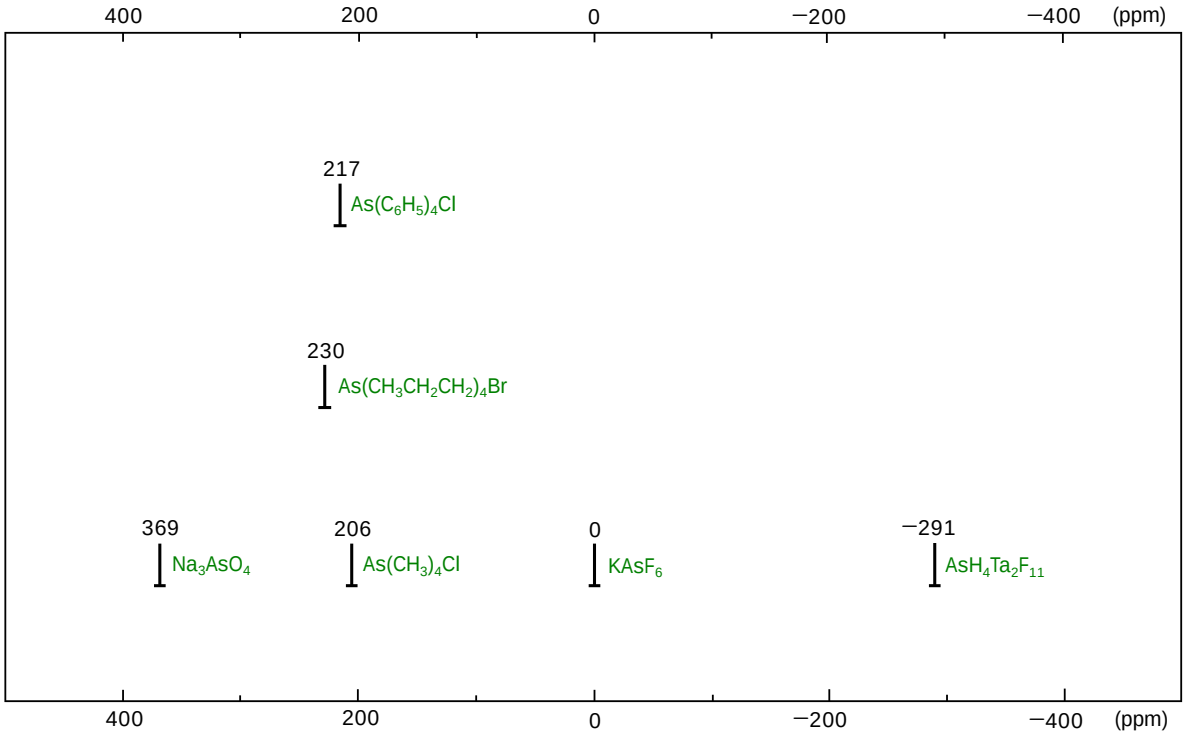

Fig. 5.17 ^{75}As chemical shifts

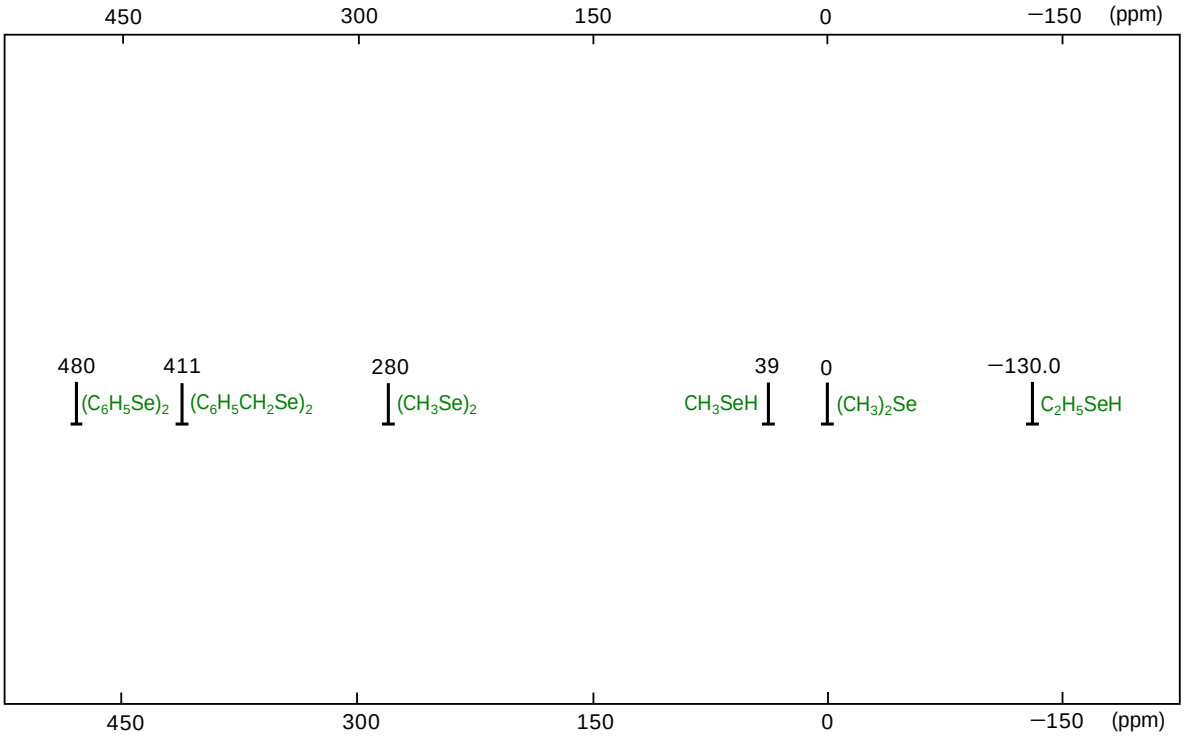

Fig. 5.18 ^{77}Se chemical shifts

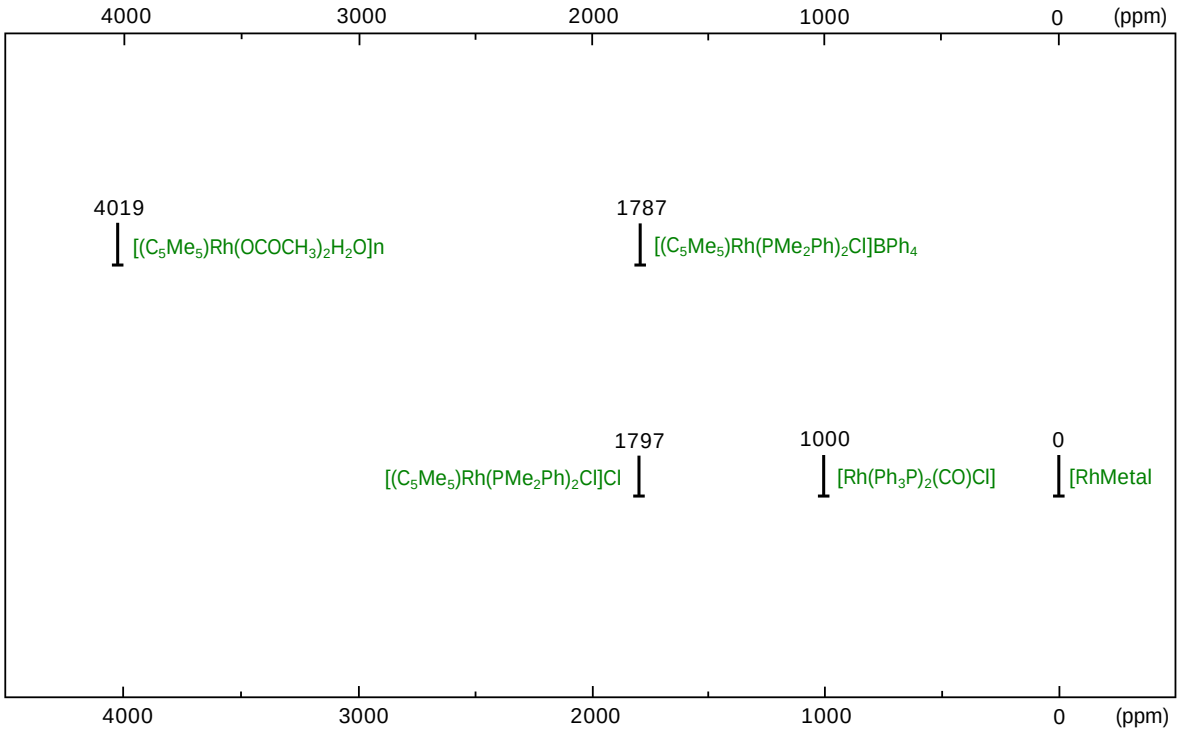

Fig. 5.19 ^{103}Rh chemical shifts

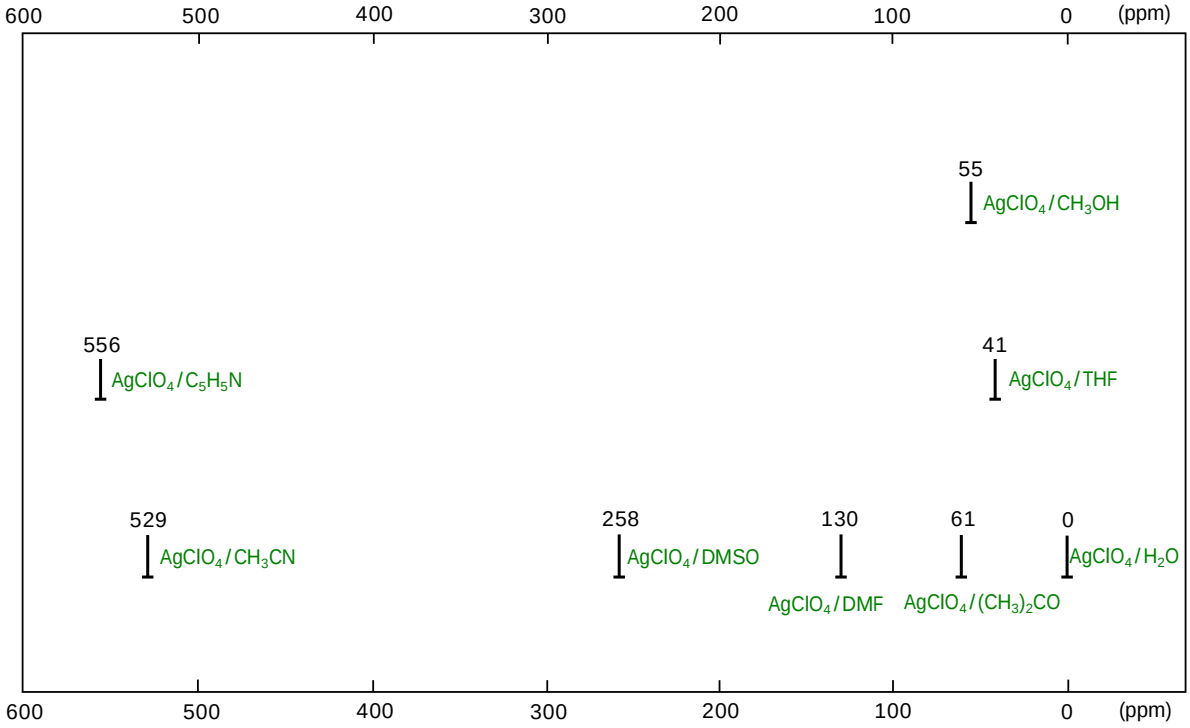

Fig. 5.20 ^{109}Ag chemical shifts

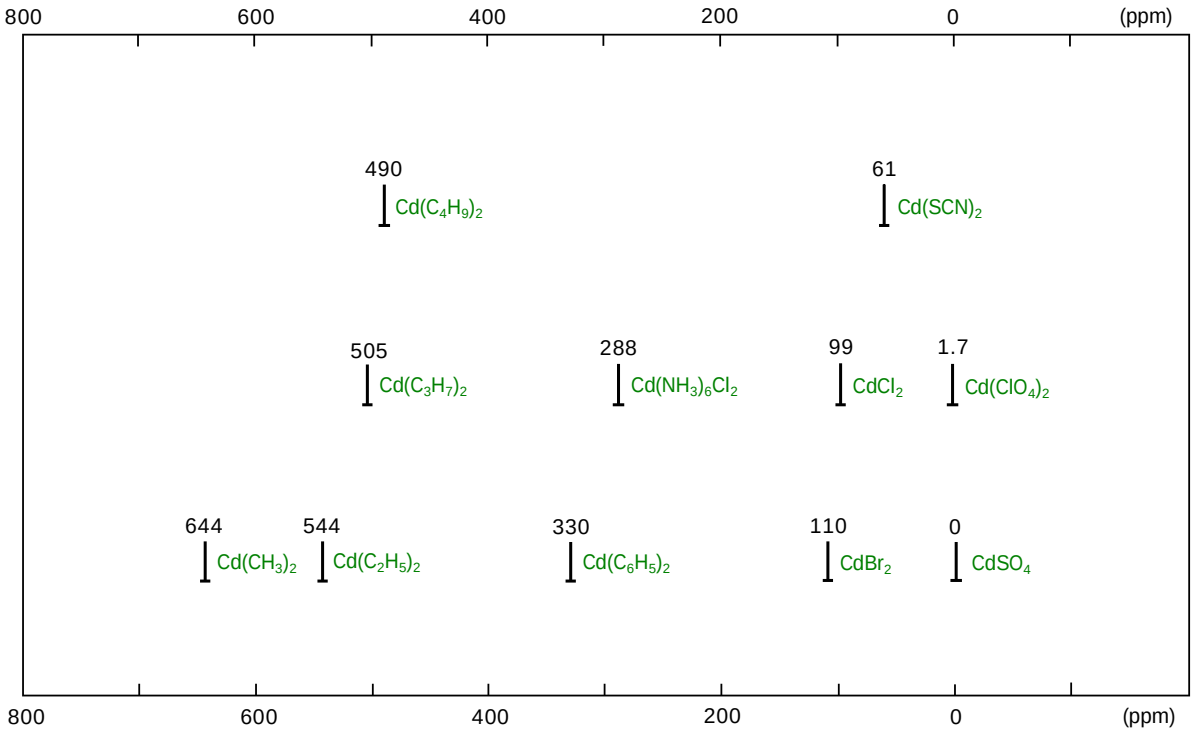

Fig. 5.21 ^{113}Cd chemical shifts

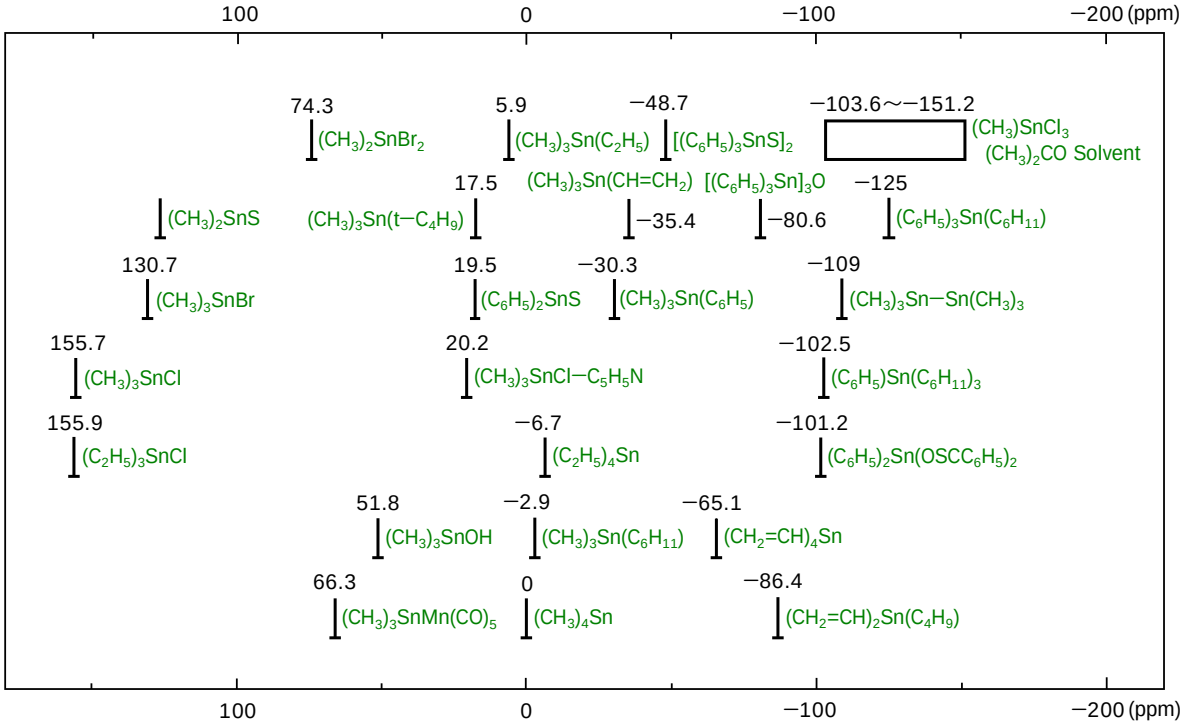

Fig. 5.22 ^{119}Sn chemical shifts

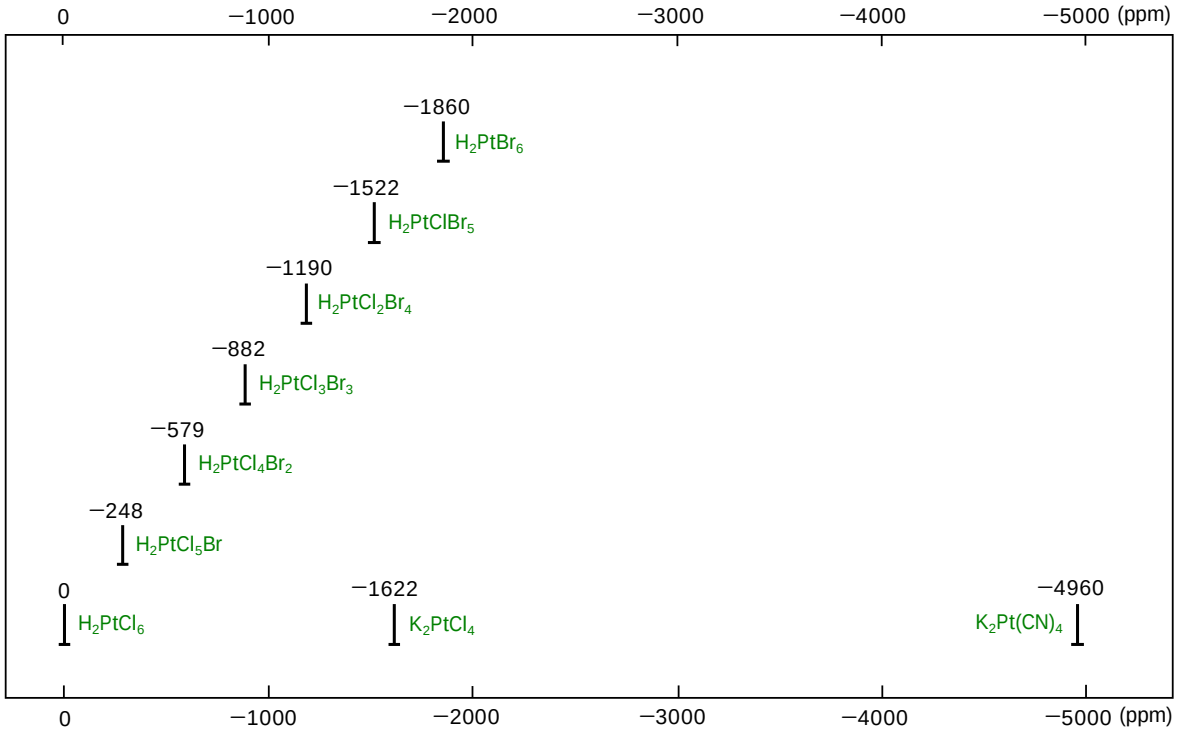

Fig. 5.23 ^{195}Pt chemical shifts

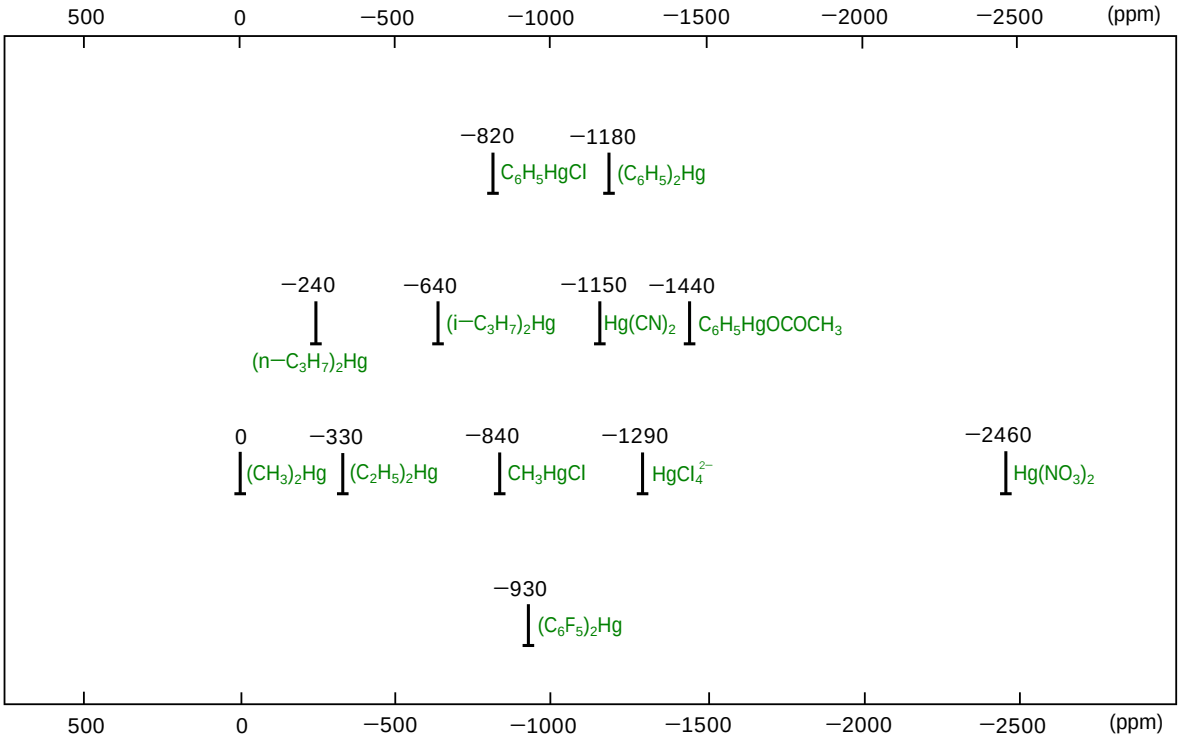

Fig. 5.24 ^{199}Hg chemical shifts

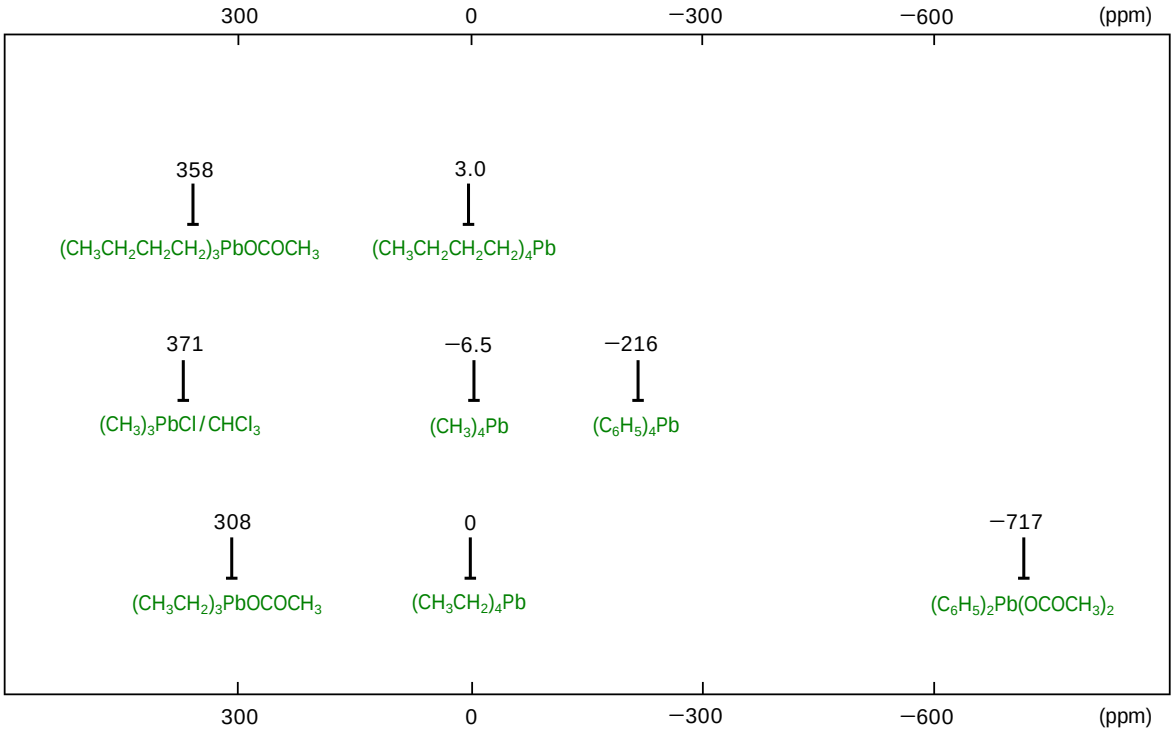

Fig. 5.25 ^{207}Pb chemical shifts

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